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**ZEOLITE IN PIG DIET:
EFFECT ON GROWTH PERFORMANCE AND AIR QUALITY**

by

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**A thesis submitted to the faculty of Graduate Studies and Research,
in partial fulfillment of the requirements for the degree of
Master of Science**

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ABSTRACT

Zeolite (77% clinoptilolite) was supplemented in grower hog rations at a rate of 2 or 5%. The growth performance (weight gain, daily consumption and feed conversion) and air quality were compared against a control group's where zeolite was replaced by fine sand. A significant reduction in the feed/gain ratio and daily consumption was observed when 2% zeolite was fed to pigs weighing less than 40 kg. The same results were obtained when 5% zeolite was fed to pigs weighing more than 50 kg. No significant difference in air quality (CO_2 , NH_3 , H_2S and temperature) was noticed between the control and the zeolite room even if the NH_3 level fell from 12.5 to 8.7 ppm when the zeolite level was increased from 2 to 5%. A slight reduction of odor intensity was observed in the zeolite room. In parallel with this research, a dynamic automated olfactometer for six panelists was conceived and built according to American and European guidelines. This instrument measures agricultural odors with precision and speed.

RÉSUMÉ

Du zéolite (77% clinoptilolite) fut ajouté à des taux de 2 et 5% dans la ration de porcs à l'engrais. Les performances alimentaires (gain, consommation et conversion alimentaire) et la qualité de l'air furent comparées aux groupes témoins où le zéolite a été remplacé par du sable fin. Une diminution significative du taux de conversion alimentaire et de la consommation journalière a été observée avec 2% de zéolite chez les porcs de moins de 40 kg et avec 5% de zéolite chez les porcs de plus de 50 kg. Aucune différence significative entre la chambre contrôle et la chambre zéolite a été notée sur la qualité de l'air (CO_2 , NH_3 , H_2S et température), bien qu'une baisse de 12.5 à 8.7 ppm du NH_3 entre l'essai à 2 et 5% fut observée dans les deux chambres. Une légère réduction de l'intensité d'odeur a été observée dans la chambre zéolite. Parallèlement à cette recherche, un olfactomètre dynamique automatisé à six panelistes a été conçu et construit selon les normes américaine et européenne. Cet appareil permet d'évaluer de façon rapide et précise, les odeurs provenant du milieu agricole.

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TABLE OF CONTENTS

ABSTRACT	i
RÉSUMÉ	ii
ACKNOWLEDGMENTS	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	vii
LIST OF FIGURES	viii
LIST OF SYMBOLS AND ABBREVIATIONS	ix
CONTRIBUTION OF THE AUTHORS	xi
 CHAPTER I	 1
Introduction	1
1.1 General Introduction	1
1.2 Problem Statement	1
1.2.1 Soil and Water Pollution	1
1.2.2 Air Pollution and Odor	3
1.3 Objectives	6
1.4 Scope	7
1.5 References	8
 CHAPTER II	 11
Literature Review	11
2.1 Soil and Water Impact	11
2.2 Air Quality and Odor Impact	13
2.2.1 Sources of Air Pollution and Odor	13
2.2.2 Odor Measurement	14
2.2.3 Air Pollution Reduction and Odor Control Methods	15
2.2.3.1 Pit Manure Additives	15
2.2.3.2 Feed Additive	16
2.2.3.3 Housing Environment	17
2.2.3.4 Manure Treatment and Storage ...	20
2.2.3.5 Manure Spreading	22
2.3 References	23

CONNECTING STATEMENT	30
CHAPTER III	31
Zeolite as a Mineral Supplement to Improve Swine Productivity and Piggery Air Quality	31
3.1 Abstract	31
3.2 Introduction	32
3.3 Literature Review	32
3.4 Objective	35
3.5 Materials and Methods	35
3.5.1 The Experimental Piggery	35
3.5.2 Experimental Material	37
3.5.3 Methodology	39
3.5.4 Statistical Analysis	41
3.6 Results and Discussion	42
3.6.1 Animal Performance	42
3.6.2 Ambient Air Quality	45
3.7 Conclusions	49
3.8 Acknowledgment	49
3.9 References	50
CONNECTING STATEMENT	54
CHAPTER IV	55
The Design of a Versatile Dynamic Olfactometer	55
4.1 Abstract	55
4.2 Introduction	56
4.3 Literature Review	57
4.3.1 Gas Chromatography to Measure Odors ...	58
4.3.2 Electro-chemical Cells	59
4.3.3 The Olfactometer	60
4.4 Conception Basis For a Dynamic Olfactometer	66
4.5 The Conception of The McGill Olfactometer	67
4.6 Summary	71
4.7 Acknowledgment	72
4.8 References	73

CHAPTER V	80
General Conclusion	80
5.1 Recommendations for Future Research	81
APPENDIX A	83
Statistical Model	83
A.1 Experimental Model	83
A.2 Classical ANOVA	84
A.3 Modified ANOVA	85
A.4 MANOVA	85
APPENDIX B	87
Growth Performance Data	87
APPENDIX C	90
SAS Code	90
APPENDIX D	92
Statistical Analysis Results	92

LIST OF TABLES

Table 3.1:	Characteristics of the experimental zeolite	37
Table 3.2:	Characteristics of the swine ration	39
Table B-1	Average Daily Gain (ADG) at 2% zeolite	87
Table B-2	Average Daily Intake (ADI) at 2% zeolite	87
Table B-3	Feed to Gain ratio (F/G) at 2% zeolite	88
Table B-4	Average Daily Gain (ADG) at 5% zeolite	88
Table B-5	Average Daily Intake (ADI) at 5% zeolite	89
Table B-6	Feed to Gain ratio (F/G) at 5% zeolite	89
Table D-1	Statistical significant levels for 2% zeolite	92
Table D-2	Statistical significant levels for 5% zeolite	92

LIST OF FIGURES

Figure 3.1	The F/G (Feed to Gain ratio), ADI (Average Daily feed Intake) and ADG (Average Daily Gain) versus weight with the feed containing 2% zeolite and 2% sand (control) (Phase 1).	43
Figure 3.2	The F/G (Feed to Gain ratio), ADI (Average Daily feed Intake) and ADG (Average Daily Gain) versus weight with the feed containing 5% zeolite and 5% sand (control) (Phase 2).	44
Figure 3.3	The over all carcass index versus carcass weight for hogs fed the zeolite and sand (control feed).	45
Figure 4.1	The octagonal arrangement of the system	68
Figure 4.2	The airflow chart of the system	70
Figure A-1	Experimental layout	83
Figure C-1	SAS code for the extrapolation of the missing value . . .	90
Figure C-2	SAS code to test the normality of the data	90
Figure C-3	SAS code to test the hypotheses with a covariable	90
Figure C-4	SAS code to test the hypotheses without a covariable . .	91
Figure C-5	SAS code to test the hypotheses by dividing the data by a covariable	91

LIST OF SYMBOLS AND ABBREVIATIONS

ADG	Average Daily Gain (kg/d)
ADI	Average Daily Feed Intake (kg/d)
ANOVA	Analysis Of Variance
ASHRAE	American Society of Heating, Refrigerating and Air Conditioning Engineers
ASTM	American Society of Testing Materials
Ca	Calcium
cdn	Canadian
CEC	Cation Exchange Capacity
CO ₂	Carbon Dioxide
COD	Chemical Oxygen Demand
Cu	Copper
DM	Dry Matter
EN	Electronic Nose
F/G	Feed to Gain ratio
H ₂ S	Hydrogen Sulfide
K	Potassium
meq	Milliequivalent
Mg	Magnesium
MANOVA	Multivariate Analysis Of Variance
MUC	Montreal Urban Community
N	Nitrogen
Na	Sodium
NH ₃	Ammonia
NH ₄ ⁺	Ammonium
NIST	National Institute of Standards and Technology
NSERC	Natural Science and Engineering Research Council of Canada
P	Phosphorus
PID	Photoionization Detector
RQMT	Règlement sur la Qualité du Milieu du Travail (Québec)
SAS	Statistical Analysis System
SD	Standard Deviation

LIST OF SYMBOLS AND ABBREVIATIONS (cont.)

SI	Smell Intensity
SiO ₄	Silica
SZA	Sodium Zeolite A
TSD-50	Signal Detection Procedure

CHAPTER I

Introduction

1.1 General Introduction

The swine industry is the third agricultural sector of importance in Canada. It represents annually 3 billion dollars of economic activity. It also represents over 20 000 producers producing more than 17 million pigs in 1996 for which over 30% came from Quebec. This industry has grown rapidly over the last few years. For example, from 1991 to 1996, the swine production has increased by 18% in Quebec, 38% in Manitoba and 8% in Canada (Statistic Canada, 1996; Statistic Canada, 1997a; Statistics Canada, 1997b). Even now, among all agricultural sectors, the swine industry is the most promising.

Several provinces plan to expand their production by 20 to 100% within the next 5 to 10 years (Dickson, 1995). This expansion is partially due to an increasing exportation demand. Canada exports 30% of its pork production annually to over fifty-five different countries. Canada is the fifth largest pork exporting country: it exports 335 000 metric tons of pork meat per year, primarily to the United States and Asian countries (Statistic Canada, 1996; Statistic Canada, 1997a). Canadian and especially Quebec's pork, is internationally recognized for its high quality.

1.2 Problem Statement

Internationally, the swine industry is faced with strong opposition from rural and urban communities. Soil, water and air pollution caused by the swine industry is being stated as the factor responsible for this opposition.

1.2.1 Soil and Water Pollution

Soil and water pollution caused by the swine industry results from poor manure storage and land disposal practices. Swine producers, in

many regions of Quebec, don't have enough land to spread their manure at a rate which does not exceed the plant's nutrients requirements. In the near future, this situation may cause many environmental problems (Ministère de l'Environnement et de la Faune du Québec, 1996). In fact, Quebec has the highest pig density in Canada: a density of 200 pigs versus 33 pigs per 100 hectares of cultivated land are reported for Quebec and Canada, respectively. In some counties of Quebec, such as in Nouvelle Beauce and Montcalm county, this density can reach 1300 to 1700 pigs per 100 hectares of cultivated land receiving manure (Statistic Canada, 1997a). Nonetheless, Quebec's situation is far from that of the Netherlands where there are 375 pigs per 100 hectares of rural and urban land (Meyer, 1997).

A study conducted by the Quebec Ministry of the Environment and Wildlife examined the capacity for agricultural land to receive animal wastes (organic fertilizer) from Quebec farms and it focused on the agricultural lands of Quebec's 9 largest river basins: Chaudière, Yamaska, L'Assomption, Etchemin, Richelieu, Saint-François, Nicolet, Bayonne, and Boyer. In these basins, where there is a dense animal population, the agricultural land is excessively fertilized in terms of phosphorus and nitrogen. If all the cultivated land of a basin could receive all its manure, it would be over fertilized in phosphorus by 183% on average in all of the river basins except for that of Richelieu. The basins would be over fertilized in nitrogen by 196% on average in 4 (Chaudière, Etchemin, Bayonne and Boyer) of the 9 studied basins. But manure was found to be applied on only 29% of the cultivated land and on top of that, farmers still use a lot of mineral fertilizer. The combined organic and mineral fertilizers applied on all the cultivated land of Quebec over fertilize phosphorus by 167% and nitrogen by 133%. On a basin scale, the study shows that it is possible to see an over fertilization of up to 460% of phosphorus and 270% of nitrogen (Ministère de l'Environnement et de la Faune du Québec, 1996).

The effects of over fertilization on the environment are different for phosphorus and nitrogen. For phosphorus, over fertilization effects

are mainly on a long-term basis. Over fertilization of phosphorus for many years, will increase the level of soil saturation and will cause leaching into rivers. Over fertilization of P is responsible for an increased phosphorus level in rivers. In many large Quebec rivers, phosphorus levels exceed, several times a year, the limit of 0.03mg/l for potential eutrophication (Simard *et al.*, 1995). The effects of nitrogen over fertilization are both short and long-term. On a short-term basis, since it is highly soluble, excess nitrogen is rapidly washed to rivers, but on a long-term basis, soluble nitrogen can reach and contaminate underground waters.

Underground water pollution caused by agricultural activities is a lurking problem for Canadians because 25 to 30% of them depend on underground water for drinking water supply. A study conducted on 1300 domestic wells in rural regions of Ontario showed that around 40% of the wells contained one or more water contaminant at a level exceeding the acceptable limit for drinking water. A correlation was found between the occurrence in wells of bacteria, specifically fecal coliforms, and the proximity of a farm where manure is routinely applied (Betcher *et al.*, 1996).

1.2.2 Air Pollution and Odor

The swine industry pollutes the air by emanating gases such as methane, hydrogen sulphide and ammonia. Methane and hydrogen sulphide are dangerous for humans and animals particularly inside swine buildings or beside manure pits. These have been known to cause many death (Schulte, 1997). Generally, methane and hydrogen sulphide are found in low concentrations and are easily removed. However, ammonia is emitted in a larger quantity and because of its environmental impact, it is more often stated as a pollutant.

Ammonia produced by the swine industry represents a large amount of the total ammonia emissions. In Denmark, the agricultural sector is responsible for approximately 93% of the total ammonia emissions (Agriculture et Agroalimentaire Canada, 1998). Kay and Lee

(1997) report that the U.K.'s agricultural sector produces around $198 \times 10^6 \text{ kg}$ of NH_3 per year, where $23 \times 10^6 \text{ kg}$ come from the swine industry. From this $23 \times 10^6 \text{ kg}$ of NH_3 , 14, 7.5, 1 and $0.2 \times 10^6 \text{ kg}$ are released by buildings, land spreading, storage and outdoor pig activity, respectively. In Denmark, where the manure tanks are generally below the building, the proportions are slightly different : 35, 20 and 40% of ammonia emissions are produced by the building, the storage and from manure spreading, respectively (Agriculture et Agroalimentaire Canada, 1998).

Ammonia emissions stay in the air for a short period of time because they fall to the ground in dry deposits or are transformed into other pollutants. From 6 to 14% fall to the ground in dry deposits directly besides the emitting sources. In Denmark, more than 85% of these deposits will occur within 100 km of the emitting source. The remaining 86 to 94% of the ammonia is transformed into ammonium nitrate and ammonium sulfate when it comes in contact with other air contaminants. Nitrate and sulfate are very small particles which remain in suspension in the air for a longer period of time than ammonia and can be transported up to 2 500 km away from the emitting source (Agriculture et Agroalimentaire Canada, 1998).

Important problems result from excessive ammonia emissions. They cause acid rain that disturb different ecosystems, damage forests, acidify fragile ecosystems and increase the risk of river and lake eutrophications (Williams and Nigro, 1997). Furthermore, ammonia emissions transformed into ammonium aerosol can, in large concentration, be harmful to human health. In the eastern part of the Fraser Valley, in British Columbia, ammonium sulfate and ammonium nitrate constituted up to 70% of the fine suspended particles in the summer air which in turn reduced visibility (Agriculture et Agroalimentaire Canada, 1998).

Ammonia is also a key ingredient in numerous odorous compounds. As a general rule, it is said that reducing ammonia emissions by 50% should reduce odor by 30% (Voermans and Verdoes, 1995). Nevertheless, odor problems are more complex than simply ammonia. In fact, odors emitted by swine production is composed of a mixture of more than 160 odorous compounds (O'Neill and Phillips, 1992). Liquid manure management for swine operations is by far the most used in Quebec and elsewhere in the world. It enhances the production of numerous odorous compounds by anaerobically degrading the remains of nutrients in the manure to, in turn, create very offensive and irritating odors.

Odor may not be universally classified because perception is dependent on human emotion and memory. A research done in Southern Michigan by Lohr (1996) demonstrated that sociological aspects influence the perception of odors. Some correlations can be drawn between various factors that influence the perception of odor. For example, the degree of annoyance towards "pig smell" is strongly decreased when the neighborhood has an economic dependance on farming. Having lived in the area for a long time, having previously met the swine facility owner or having the impression that the owner is making efforts to reduce the odor problem are factors which decrease the perception of odor as a nuisance. Moreover, the negative perception of odor and the annoyance with an odor is greater when the neighborhood area is categorized as residential, sub-urban or small town. Those who think that odor is a nuisance generally declare that the odor episode is longer and more frequent than those who find that swine odor is not a problem. Nevertheless, all Southern Michigan residents surveyed during this study, declared that they have not and do not plan to directly complain about the odor problem. Nonetheless, they will support any zoning regulation that will restrict the expansion of the swine industry in their region (Lohr, 1996).

Odors are hard to deal with because of their intangible nature. Very few regulations legislate odors because there is no standard way

of measuring them. The interaction of the different odorous compounds are so complex that it is almost impossible to analyze them analytically. The human nose, with its 10 to 30 million receptor cells in 4 cm², is still the most efficient odor sensor (Li *et al.*, 1997). No electronic device such as an electronic nose, gas chromatograph and photoionization detector until now, can simulate the human olfactory sense at an acceptable workable level. The olfactometry method uses the power of the human nose to evaluate the concentration of odors. An olfactometer determines the threshold level for a specific odor by diluting odors below the human threshold level and then increasing the odor concentration until the odor is detected by a panelist. Henceforth, an odor unit can be defined as the number of dilutions required for 50% of the population to detect the odor. This odor unit can be used to compare and handle different odor problems. The olfactometer is gaining more and more recognition around the world and is starting to become a reference method for many odor related work.

1.3 Objectives

The dietary inclusion of zeolite was studied as an economically viable solution to reduce the environmental impact of the swine industry. The objectives of this study were to measure the effects of adding zeolite (77% clinoptilolite) as mineral supplement in the ration of grower hogs.

Supplementing feed with two levels of zeolite, 2 and 5% on dry matter basis, the following parameters were compared:

1. The average daily feed consumption of the pigs
2. The average daily gain in body weight of the pigs
3. The feed to gain ratio of the pigs
4. The carcass quality of the pigs
5. The ambient room NH₃ and H₂S levels
6. The ambient room odor intensity

In parallel with the first objective, an olfactometer was conceived and built to evaluate odor concentrations in agricultural buildings. The olfactometer was not used to evaluate the effect of zeolite on odor levels

in piggeries, because the instrument was not ready for use at the time of the trial.

1.4 Scope

The results obtained in this study are limited to two levels of zeolite in the diet: 2 and 5%. A regular low energy and 16% protein pallet ration was supplemented with 2 or 5% zeolite, without balancing the energy and protein levels. Fine silica sand was added at the same level as zeolite in the control diet. Also, the 2 and 5% trial was limited to respectively 60 and 54 pigs fed with the zeolite diet and respectively 60 and 54 pigs fed with the control ration. Each trial was limited to 8 weeks. At the beginning of each trial, the pigs had a variety of weights and ages. Nevertheless, the pigs were sorted into two groups (zeolite and control) of similar weight repartition with the same number of males and females in each group. The results pertained to pigs weighing from 25 to 100 kg. The study is limited to the effects on animal growth performance and ambient air quality. The mineral analysis of the feces as well as the nutrient balance for each individual pig was not included in the study.

The automated olfactometer was built in accordance to the American (ASTM) and the European (CEN) standard for the forced choice triangular method. The number of panelists seated was limited to 6, but up to 24 panelists can run a test in sequential runs of 6 panelists. The dynamic dilution was compared against NIST traceable flow calibrators. The n-butanol concentration of the butanol injector was obtained by gas chromatography. No real odor evaluation was made with this olfactometer.

1.5 References

Agriculture et Agroalimentaire Canada. 1998. Stratégie de recherche sur la gestion du lisier de porc au Canada, Catalog no. A42-77/1998F. Ministre des Approvisionnements et Services Canada, Ottawa, Canada.

Betcher, R.N., Rudolph, D.L. and Nicholson, R. 1996. Impact of agricultural activities on groundwater quality. In: Manure Management Symposium Proceedings. Winnipeg, Canada, 53-62.

Dickson, A. 1995. Issues we face in developing Manitoba's livestock potential. In: Manure Management Symposium Proceedings. Winnipeg, Canada, 19-26.

Kay, R.M., and Lee, P.A. 1997. Ammonia emission from pig buildings and characteristics of slurry produced by pigs offered low crude protein diets. In: Proceedings of the International Symposium on Ammonia and Odour Control from Animal Production Facility. Vinkeloord, The Netherlands, 253-260.

Li, X.W., Bundy, D.S. and Hoff, S. 1997. Developing an olfactometer for livestock odor evaluation. In: Manure Management Symposium Proceedings. Winnipeg, Canada, 155-160.

Lohr, L. 1996. Factors related to odour perceptions and annoyance in a rural context. In: Manure Management Symposium Proceedings. Winnipeg, Canada, 45-61.

Meyer, Th.A.M. 1997. Ammonia Control in Agriculture. In: Proceedings of the International Symposium on Ammonia and Odour Control from Animal Production Facility. Vinkeloord, The Netherlands, 575-577.

Ministère de l'Environnement et de la Faune du Québec. 1996. Document de réflexion sur la capacité des sols du territoire québécois à supporter les élevages. Unpublished document of "la table de concertation sur le projet de règlement sur la réduction de la pollution d'origine agricole". Quebec, Canada.

O'Neill, D.H. and Phillips, V.R. 1991. A review of the control of odour nuisance from livestock buildings: Part 1, Influence of the techniques for managing waste within the building. *Journal of Agricultural Engineering Research*, 50: 1-10.

O'Neill, D.H. and Phillips, V.R. 1992. A review of the control of odor nuisance from livestock buildings: Part 3, Properties of the odorous substances which have been identified in livestock wastes or in the air around them. *Journal of Agricultural Engineering Research*, 53: 23-50.

Schulte, D.D. 1997. Critical parameters for emissions. In: *Proceedings of the International Symposium on Ammonia and Odour Control from Animal Production Facility*. Vinkeloord, The Netherlands, 23-32.

Simard, R.R., Cluis, D., Gangbazo, G. and Beauchemin, S. 1995. Phosphorus status of forest and agricultural soils from a watershed of high animal density. *Journal of Environ. Qual.*, 24(3): 420-425.

Statistics Canada. 1996. *Agricultural Financial Statistics*, Catalog no. 21-205-XPB. Statistic Canada, Ottawa, Canada.

Statistics Canada. 1997a. *Agricultural Profile of Quebec*, Catalog no. 95-176-XPB. Statistic Canada, Ottawa, Canada.

Statistics Canada. 1997b. *Faits saillants nationaux et provinciaux du recensement de l'agriculture de 1996*, Catalog no. 93F0033-XIF. Statistic Canada, Ottawa, Canada.

Voermans, J.A.M., Verdoes, N. 1995. Reduction of ammonia emission from pig barns. In: Proceedings '95 of International Livestock Odor Conference '95. Iowa State University, Ames, Iowa, Usa, 140-144.

Williams, A.G. and Nigro, E. 1997. Covering slurry stores and effects on emissions of ammonia and methane. In: Proceedings of the International Symposium on Ammonia and Odour Control from Animal Production Facility. Vinkeloord, The Netherlands, 421-428.

CHAPTER II

Literature Review

The following chapter will discuss different solutions used to reduce the environmental impacts of the swine industry. Amongst all the possible solutions presently available or proposed to the producer, only those which are efficient and economically viable are susceptible to be accepted and used, because swine producers are in a tight cash situation. The following solutions will be divided into two main categories: solutions to control or limit the impact on soil and water, and solutions to control the air quality, especially the odor and ammonia emissions.

2.1 Soil and Water Impact

Soil and water pollution resulting from the swine industry, are mainly due to the excessive rate of manure applied to cultivated land. Swine manure N, P and K content must be reduced in order to control the environmental impact related to manure applications. Better feed management can reduce the amount of manure and can decrease its nutrient content.

Several research projects have been conducted to try to reduce the amount of total nitrogen and ammonia in the feces. Sutton *et al.* (1997) fed growing-finishing pigs with a low crude protein (10%) diet supplemented with synthetic essential amino acids and 5% cellulose to reduce the fresh manure's ammonia content by 68%. It also reduced the manure's total nitrogen by 60% and increased the dry matter content of the manure by 50% compared to the control group fed a regular 13% crude protein commercial ration. Kay and Lee (1997) showed that it is possible to reduce the volume of slurry by 28% and decrease its nitrogen content by 40% by feeding a low crude protein (16.5%) diet supplemented with synthetic essential amino acids instead of feeding a regular commercial 22.5% crude protein diet. These studies

demonstrated that synthetic amino acid supplements can reduce manure N levels : however, the cost of these synthetic amino acids makes this option less attractive. Lee and Kay (1997) calculated that the use of low crude protein supplements increases the operating cost by 20%, even if the reduction of feed intake and manure volume are considered.

Other growth promoters such as antibodies, hormones and beta-agonist are used to reduce the nitrogen and phosphorus excretions (Baidoo, 1996). Williams and Kelly (1994) reported that feeding ractopamine (beta-agonist) and porcine somatotropin to a finishing pig, can increase the feed efficiency by 0.54 and 1.04 kg feed/kg gain respectively and decrease the amount of manure produced by 0.68 and 1.61 kg of DM per finished pig, respectively. While the results prove the efficiency of growth promoters, they are not accepted by society and consumers.

The pig's feed efficiency can be enhanced by increasing the digestibility of the feedstuffs such as feeding different sources of phosphorus. In general, the phosphorus supplied by cereal grains has a low digestibility of 20% to 40%. The remaining 60 to 80% of the phosphorus is excreted in the feces. In contrast, the organic phosphorus in meat and bone meal and the inorganic phosphorus in monocalcium phosphate and dicalcium phosphate have a higher digestibility of 70 to 80% (Jongbloed and Lenis, 1992).

The digestibility of feed can be enhanced by supplemental feed enzymes. The supplemental enzymes support the animal endogenous enzymes or supply non-existent enzymes in the digestive tract of the animal to degrade feed components. Cellulase and phytases have been used to increase the digestibility of nitrogen and phosphorus. Jongbloed *et al.* (1991) showed that phytase, in a corn- soybean-wheat pig ration, can increase the digestibility of the phosphorus by 36%. Furthermore, Williams and Kelly (1994) reported that phytase can reduce nitrogen and phosphorus content in manure by 5%. They also reported that cellulase decreases nitrogen and phosphorus by 5 and 25-30%

respectively. An increase of feed efficiency can be achieved by microbial enzymes inclusion in a hullless barley diet. Pigs of 8 to 20 kg, 20 to 40 kg, 40 to 60 kg, fed with this diet, revealed an increase feed efficiency of 10, 5.3, and 3.0%, respectively (Baidoo, 1996).

Zeolite can also be fed as mineral supplement to increase feed efficiency, reduce ammonia volatilization and control odors. Zeolite is an aluminosilicate (a volcanic clay) with a high cation exchange capacity. Some types of zeolite such as clinoptilolite have an affinity for nitrogen and sulphur compounds (Barrington and El Moueddeb, 1995). Fed to growing finishing pigs at 5%, zeolite is known to adsorb the harmful ammonia produced by the intestinal bacteria and slows down the passage of feed to the intestinal tract. Barrington and El Moueddeb (1995) obtained a better net feed conversion of 0.29 kg of feed per kg of weight gain. This better feed conversion is expected to reduce the amount of manure produced and to decrease its nutrient concentration. Also, zeolite was observed to reduce ammonia volatilization by 75% on average and decrease odor levels by 1 point on a scale of 0 to 5 (Barrington and El Moueddeb, 1995). Zeolite was also found to be interesting because its benefits overcame its costs by \$7.75 per finished pig (Barrington, 1996).

2.2 Air Quality and Odor Impact

2.2.1 Sources of Air Pollution and Odor

Ammonia volatilization is the main source of air pollution and is closely related to odor. The rate of ammonia volatilization is a function of the dissolved ammonia in the manure and the manure air contact area. Ammonia emissions start right after the manure is excreted and continue after it is spread on land. Manure odors are worst with liquid handling systems resulting in anaerobic conditions. The anaerobic decomposition of swine manure produces many chemically reduced and obnoxious gases which are very offensive. This anaerobic degradation starts within 24 hours of excretion. The concentration of malodorous compounds increases dramatically from fresh manure to manure stored

anaerobically for 24 hours: phenol increases by 140%, indole by 160% and total sulphide by 1350% (O'Neill and Phillips, 1991). Therefore, odors are reduced by reducing the time that manure is left inside the building. Guingand *et al.* (1997) showed that odor emissions were reduced by 50% when manure was not stored below the slotted floor.

Controlling ammonia emissions and odors can be achieved in different ways: by controlling the pig's diet, controlling the building environment, applying different manure treatments, improving the design of manure storage tanks and finally, using less odorous spreading methods. But, before evaluating any method, an effective odor measurement device is required.

2.2.2 Odor Measurement

Swine manure odors are composed of numerous compounds such as carboxylic and phenolic acids, aldehydes, esters, sulphide, thiols, amines and nitrogen heterocycles. O'Neill and Phillips (1992b) have reported 168 different compounds responsible for swine odors. Over 30 of these compounds have an odor detection threshold at a concentration under or equal to 0.001 mg/m³. The compounds with the lowest detection threshold generally contained sulfur (O'Neill and Phillips, 1992b).

Hobbs *et al.* (1995) compared different methods to assess odor from swine and poultry slurries. Photoionization detectors (PID) and electronic noses (EN) based on a polypyrrole sensor were evaluated against a standard force choice olfactometry method. PID and EN showed some potential to evaluate odor from swine and poultry slurries, but they are still one thousand times less sensitive than the olfactometry method. Also, the results obtained with PID and EN can be different from one farm to another since these device detect only some but not all odorous compounds as an indication of the odor level. Different odorous compounds other than those detected by the device will not appear in the results (Hobbs *et al.*, 1995). Olfactometry still is the most accurate way to measure agricultural odors. A wider review

of odor measurement methods will be present in chapter IV of this document.

2.2.3 Air Pollution Reduction and Odor Control Methods

2.2.3.1 Pit Manure Additives

Many manure additives are sold on the market. They can be classified into 5 different categories: masking agents, counteractants, digestive deodorants, adsorbents and chemical deodorants.

Masking agents and counteractants treat the odors in a similar way. Masking agents are a mixture of aromatic oils used to cover-up the undesirable odors by a more desirable one (Swine Odor Task Force, 1995). In some cases, these masking agents can be effective on a short-term base to control odors. On a longer term, these compounds are quickly broken down by the bacterial activity in lagoons or storage tanks. Nevertheless, some studies showed that masking agents were in general more effective than digestive deodorants (Burnett and Dundero, 1970).

Counteractants are made-up of a mixture of aromatic oils that cancel or neutralize odors so that the intensity of the mixture is less than that of the constituents (Ritter, 1989).

Digestive deodorants are made-up of bacteria and enzyme that eliminate odors through a biochemical digestive process (Ritter, 1989). Many of these products have been commercialized during the past years. These compounds are not only sold to control odors but to enhance solid breakdown and nitrogen conservation. Under laboratory conditions, Zhu *et al.* (1997) observed that it is possible to reduce the threshold of odors by 83 to 97%. Ritter (1989) found that digestive deodorants work when the bacteria added predominate in the manure. Under laboratory conditions, some products work well in drums of 106 or 208 liters: however, in the field, manure handling conditions change and these bacteria die off before they become predominant.

Adsorbents are products with a large surface area adsorbing the odors before they are released into the environment (Ritter, 1989). Some examples of these adsorbents are sphagnum peat moss, limestone and zeolite (Swine Odor Task Force, 1995). Airolidi *et al.* (1993) showed in a laboratory test that 10% zeolite (equal to 30.8 g/l of manure) is needed to significantly decrease by 33% the emission of ammonia produced by manure. Adsorbents work efficiently only when used in large quantities and they are often too expensive.

Chemical deodorants are strong oxidizing agents or germicides altering or eliminating bacterial action responsible for odor production (Ritter, 1989). Oxidizing agents chemically reduce odorous compounds into less offensive ones (Ritter, 1989). Hydrogen peroxide, potassium permanganate, ozone, orthodichlorobenzene chlorine formaldehyde and paraformaldehyde have been tried to reduce odors. Hydrogen peroxide at 100-125 ppm has been found to be most economical (Ritter, 1989). Zhu *et al.* (1997) showed in a laboratory test, that some chemical oxidizing agents are able to reduce the odor threshold by 58%. Also, Berg and Hörnig (1997) added 5% lactic acid (50% concentrated) by volume in manure to reduce its pH to 4.5. This decreased the ammonia and methane emissions by nearly 90%. So in general, reducing compounds must be applied frequently in large and costly amounts to control odors in a lagoon or manure tank (Ritter, 1989). Furthermore, these chemicals are often corrosive and harmful to the environment.

2.2.3.2 Feed Additives

Not all pig manure has the same odor production potential. As a general rule, nitrogen is the basic ingredient in ammonia and many odorous compounds. When the amount of protein in the diet is poorly balanced or protein is fed in excess, the animal rejects this excess through its feces. Improving the pig's feed efficiency, reduces the amount of nitrogen rejected in the feces and thus reduces potential odors. In general, if nitrogen in the feces is reduced by 100 units, the odor level will be decreased by 75 units (Swine Odor Task Force, 1995). Feed efficiency can be improved in four different ways: by adding

essential amino acids, increasing the digestibility of proteins and adding odor absorber, enzyme and microbes.

By substituting synthetic amino acids for traditional protein sources, the amount of nitrogen excreted by pigs can be decreased substantially. Amino acids reduced the ammonia emissions by 40% and thus diminishing the odor emissions by 30%. However, these techniques are expensive and more research is needed in this field before they can be used commercially (Swine Odor Task Force, 1995; Lee and Kay, 1997).

Different studies showed that it is possible to improve the digestibility of proteins by using a better processing or rendering technique. Enzymes such as cellulases and phytases have been reported to reduce by 5% the amount of nitrogen in the manure (Williams and Kelly, 1994). In another study, the use of proteolytic enzymes in feed processing and dietary supplements in the diet have been found to improve protein digestibility (Swine Odor Task Force, 1995).

Odor absorbent added to the pig's diet, have been evaluated. Calcium bentonite, sagebrush, charcoal and zeolite were used for their potential to absorb ammonia produced in the intestinal tract. Zeolite is particularly used because of its high cation exchange capacity. In some cases, this cation exchange can reach 500 meq/100g (Mumpton and Fishman, 1977). Although over 45 different zeolites are available, some such as chabasite, phillipsite, and clinoptilolite are more promising as feed supplement because of their specific attraction for ammonia (Sersale, 1983). Absorbents not only reduce ammonia in feces, but in some cases, increase the pig's feed efficiency. A review of the research done in this field is presented later in chapter III.

2.2.3.3 Housing Environment

By controlling dust, ammonia, and hydrogen sulfide inside swine housings, odor emissions have been reduced. Different ways have been explored to control these factors.

Malodorous gases such ammonia and hydrogen sulphide as well as respirable dust can, at certain levels, cause various health problems for pigs and workers (Donham, 1989). The safe level of these gases and dust is frequently exceeded in swine facilities (Donham, 1989, Donham and Popendorf, 1985, Donham, 1990). Seedorf (1997) reported that out of 83 livestock shelters in Germany, nearly 58% had dust levels exceeding health safety standards. Quebec has regulations concerning the quality of the work environment. These regulations set the maximum limit for ammonia, hydrogen sulphide and total dust at 25 ppm, 10 ppm and 10 mg/m³, respectively (RQMT, 1994). However, some researchers report respiratory problems among swine workers exposed to ammonia and total dust levels of 7.5 ppm and 2.5 mg/m³ (Reynolds *et al.*, 1996). Pigs are also affected by the quality of environmental conditions. Using an electrostatic precipitator filter, Lau *et al.* (1996) obtained an increase of 0.04 kg/day in daily gain by decreasing the level of dust by 20 to 52% in finishing hog rooms. They also observed that the incidence of lung score was 35 to 40% lower and snout score was 25 to 40% lower in the filtered room compared to the unfiltered room. Furthermore, a laboratory scale test showed that odor threshold was decreased by 75% when 100% of the dust was removed from the exhaust air of the piggery (Hoff *et al.*, 1997). When odors are reduced in swine housing facilities, the dust, ammonia and hydrogen sulphide are also reduced and workers, pigs and neighbors benefit.

An alternative way to control dust is to use oil in the feed and on the floor. Perkins and Feddes (1996) have applied mineral oil to the floors of a swine farrowing unit at a level of 24 ml/m² weekly. They have been able to reduce dust by 73% during a 24 hour period following the application of oil. Also, Takai *et al.* (1993) applied daily 5 to 15 ml of rapeseed oil per pig on floors of a piglet room to reduce the respirable dust by 76%. Zhang *et al.* (1994) reduced the respirable and inhalable dust by 75%, by applying a mineral oil to the floor of a grower finishing unit. Chiba *et al.* (1985-1987) reduced the aerial dust by 21 to 53% by adding tallow to the pig's ration at a level of 2.5 and 7.5%. Gore *et al.* (1986) added 5% soyabean oil to a starter diet to reduce the settled dust

concentration by 45%.

A pit ventilation system can be used to control dust and air contaminants. This system should be able to decrease the total bacteria, ammonia and dust if the ventilation rate is high enough. In a 2 year study, conventional ventilation and pit ventilation were compared in a swine gestation building. This system was not able to reduce the bacteria at the RQMT recommended level. The gram-negative bacteria were 8 to 41 times higher than the recommended level (Lavoie *et al.*, 1997). Furthermore, Choinière *et al.* (1997) found that pit ventilation in finishing pig units, compared to a conventional wall mount ventilation, increased ammonia emissions by 100% during summer and 20-30% during winter, under Quebec conditions.

Odor emanating from a piggery can be controlled by methods such as a biofilter, a bioscrubber, a thermal incinerator, a catalytic incineration, an absorption system and diffusion chimneys. The principle of a biofilter and bioscrubber is to pass odorous air through a filter containing biological materials (peat, compost and soil) able to breakdown volatile compounds into carbon dioxide, water and other harmless products. This method can remove 90% or more of the volatile organic compounds and is efficient in treating low concentrations of odorants (Swine Odor Task Force, 1995). Hoff *et al.* (1997) show that a low cost biomass filter made of chopped corn stalks and cobs can effectively remove 21 to 90% of dust particles below 5 and 10 microns respectively and reduce odor threshold by 23 to 47%. Young *et al.* (1997) used a pilot-scale biofilter made of a 3 to 1 mixture of yard waste compost and wood chips which reduced the odor intensities by 61% in a swine gestation building. Dong *et al.* (1997) used a microbe seeded wet bioscrubber to remove up to 54% of the ammonia contained in the exhaust air of piggeries. The cost of a biofilter and a bioscrubber often exceed the benefits. Siemers and Van den Weghe (1997) concluded that the wet scrubber and biofilter were expensive and should be used as a last resort.

Thermal and catalytic incineration use temperatures of 700 and 400 °C respectively to oxidize odorous compounds. The absorption principle is one of the techniques that requires that air be passed through a filtration media such as activated carbon (O'Neill *et al.*, 1992a). Finally, another way to deal with odors emanating from buildings, is to dilute the odorous compound in the atmosphere by using a well designed diffusion chimney. The height of the chimney is a function of the ventilation rate and the odor concentration. O'Neill *et al.* (1992a) estimated that a chimney 24 m in height is able to disperse the odor below its nuisance level. Chimneys, bioscrubbers and biofilters can cost between 7 to 10 \$ per finished pig, and are thus the least costly methods to control emanating odors from swine buildings. Thermal and catalytic incineration and absorption can cost from 105 to 425 \$ per finished pig and are too expensive (O'Neill *et al.* 1992a).

2.2.3.4 Manure Treatment and Storage

Manure can be treated while in storage and before it is disposed of on the land. Different ways can be used to treat manure such as composting, aeration, anaerobic digestion, aerobic digestion and biological filtration. Each method has its advantages.

Non aerated lagoons are shallow storage facilities widely used in Southern US because they are the cheapest ways to handle manure. Solid degradation is promoted by the microbial activity as long as the manure temperature is above 20 °C. Undisturbed, the lagoon will not produce a lot of odors. But, when it's mixed and pumped, it will release very offensive odors. The manure that comes out of these lagoons is also very odorous when it is spread on the land.

Anaerobic digestion can produce less offensive odors from slurries along with methane. Massé *et al.* (1997) used a laboratory scale batch wise psychrophilic anaerobic digester to treat swine manure. With this treatment, COD was reduced by up to 73% and the manure was relatively odorless. Psychrophilic anaerobic digestion can produce up to 0.66 litres of methane per gram of volatile solid fed to the digester in

a biogas mixture containing methane at a level of 50 to 80% of methane (Massé *et al.*, 1997).

Aerobic digestion is also possible to treat swine slurry and decrease odors. The effectiveness of the aerobic digestion is a function of residence time and slurry dry matter content. Sneath *et al.* (1992) used a farm scale aerobic digester to reduce odors by 70%. A 1.5% dry matter slurry is aerobically treated during four days to produce a stable odorless slurry for up to 30 days. Often, it is economical to separate the solid and liquid portions of the slurry before it is aerated. Sneath (1988) showed that the higher the level of dry matter in the slurry, the cheaper it is to centrifugally separate and aerobically treat the manure, especially for large herds. Aerobic digestion will deodorize manure at a cost of 1.5 to 2 \$ per pig, for a large herd. The solid portion should be composted or land spread.

Manure tank covers reduce odor, ammonia and hydrogen sulfide production by 90%(Agriculture et Agroalimentaire Canada, 1998; Rodd, 1998, Bundy *et al.*, 1997). Lee Whittington of the Prairie Swine Center tested a balloon-type cover to reduce odor emissions by more than 95%. This balloon-type cover costs about \$10 000 cdn for a 23 meter diameter concrete tank (Prairie Swine Center, 1997). Bundy *et al.* (1997) tried different covering materials on manure tanks and concluded that biological covers (15 to 25 cm of chopped corn stalks or straw) are effective and inexpensive but tend to sink to the bottom of the tank during the winter. A floating Leka rock layer of 4 to 8 cm offers excellent odor control all year round. It can even be partially reused but it is expensive (\$150-\$180 U.S. per m³). A low density polyethylene mesh with a liquid film on the surface does not effectively control odors. Finally, a surface foam produced by bubbling air through the manure once every three days seems to offer an interesting alternative but requires further testing.

Biological filters can integrate the treatment of manure and air vented from swine buildings. First, the manure liquid and solid

fractions are separated. Then, the liquid fraction is treated using a biological filter of peat moss and bark chips. The exhaust air of the swine building is circulated through the biological filter as aeration system. The solid fraction is composted or land spread (CRIQ, 1998). Such biofilters cost approximately \$10 per finished hog.

2.2.3.5 Manure Spreading

Land disposal of livestock wastes produce a lot of odor by disturbing the manure and enhancing its contact with ambient air. In fact, 70% of complaints concerning pig odor come from manure spreading (Swine Odor Task Force, 1995). Another 10 % concerns the odorous air emanated from the swine building and the remaining 20% concerns the storage facility (Agriculture et Agroalimentaire Canada, 1998). To reduce odor emissions and ammonia volatilization, manure is spread as close as possible to the ground or, even better, is directly incorporated into the soil. Morken and Sakshaug (1997) showed that using their new direct ground injector made it possible to inject manure into the soil to a depth of 5 to 10 cm. This new injector pressurizes the manure into a series of 13mm nozzles placed directly on the ground. As a result, ammonia volatilization is decreased by up to 90% and all possible sources of run-off are removed.

2.3 References

Agriculture et Agroalimentaire Canada. 1998. Stratégie de recherche sur la gestion du lisier de porc au Canada, Catalog no. A42-77/1998F. Ministre des Approvisionnements et Services Canada, Ottawa, Canada.

Airoidi, G., Balsari, P. and Chiabrando., R. 1993. Odour control in swine houses by the use of natural zeolites: First approach to the problem. In: Livestock Environment IV, Fourth International Symposium, ASAE. St-Joseph, Michigan, USA, 701-708.

Baidoo, S.K. 1996. Manure modifications through dietary manipulation: Dietary effect on volume, content and odour. In: Manure Management Symposium Proceedings. Winnipeg, Canada, 161-168.

Barrington, S.F. 1996. Practical methods for controlling odors. In: Manure Management Symposium Proceedings. Winnipeg, Canada, 149-158.

Barrington, S.F. and El Moueddeb, K. 1995. A direct method for the evaluation of odors. Proceeding International Conference on Livestock odors, Iowa State University. Ames, Iowa, USA, 65-69.

Berg, W. and Hörnig, G. 1997. Emission reduction by acidification of slurry - Investigations and assessment. In: Proceedings of the International Symposium on Ammonia and Odour Control from Animal Production Facility. Vinkeloord, The Netherlands, 459-466.

Bundy, D.S., Li, X.W. and Hoff, S.J., 1997. Malodour abatement by covering materials. In: Proceedings of the International Symposium on Ammonia and Odour Control from Animal Production Facility. Vinkeloord, The Netherlands, 101-110.

Burnett, W.E. and Dundero, N.C. 1970. Control of odors from animal wastes. Transaction of the ASAE, 13: 221-224.

Chiba, L.I., Peo, E.R. Jr., Lewis, A.J., Brumm, M.C., Fritschen, R.D. and Crenshaw, J.D. 1985. Effect of dietary fat on pig performance and dust levels in modified open front and environmentally regulated confinement building. *Journal of Animal Science*, 64: 763-781.

Chiba, L.I., Peo, E.R. Jr. and Lewis, A.J. 1987. Use of dietary fat to reduce dust, aerial ammonia and bacterial colony forming particle concentrations in swine confinement buildings. *Transactions of the ASAE*, 30: 464-468.

Choinière, Y., Marquis, B. and Gingras, G. 1997. Ammonia and contaminant concentrations with conventional versus pit ventilation in finishing pig units. In: *Proceedings of the International Symposium on Ammonia and Odour Control from Animal Production Facility*. Vinkeloord, The Netherlands, 365-372.

CRIQ, 1998. Le Biosor^{mc}-Lisier. Centre de Recherche Industrielle du Québec, Canada. Internet document published by the CRIQ, Canada.

Dong, L., Heber, A.J., Patterson, J.A., Strobel, B.R., Jones, D.D. and Sutton, A.L. 1997. Bioscrubber for removing ammonia from swine house exhaust air. In: *Proceedings of the International Symposium on Ammonia and Odour Control from Animal Production Facility*. Vinkeloord, The Netherlands, 529-532.

Donham, K.J. and Pependorf, W.J. 1985. Ambient levels of selected gases inside swine confinement buildings. *American Industrial Hygiene Association Journal*, 46: 658-661.

Donham, K.J. 1989. Agricultural occupational and environment health: Police strategies for the future. *Applied Occupational and Environment Hygiene*, 4(10): F12-F22.

Donham, K.J. 1990. Health effects from work in swine confinement buildings. *American Journal of Industrial Medicine*, 17: 17-25.

Gore, A.M., Kornegay, E.T. and Viet, H.P. 1986. The effects of soybean oil on nursery air quality and performance of weaning pigs. *Journal of Animal Science*, 63:1-7.

Guingand, N., Granier, R. and Massabie, P. 1997. Characterization of air extracted from pig housing: effect of the presence of slurry and ventilation rate. In: *Proceedings of the International Symposium on Ammonia and Odour Control from Animal Production Facility*. Vinkeloord, The Netherlands, 49-55.

Hobbs, P.J., Misselbrook, T.H and Pain, B.F. 1995. Assessment of odors from livestock wastes by a photoionization detector, an electronic nose, olfactometry and gas chromatography-mass spectroscopy. *Journal of Agricultural Engineering Research*, 60: 137-144.

Hoff, S.J., Bundy, D.S. and Li, X.W. 1997. Dust effects on odor and odor compounds. In: *Proceedings of the International Symposium on Ammonia and Odour Control from Animal Production Facility*. Vinkeloord, The Netherlands, 101-110.

Jongbloed, A.W. and Lenis, N.P. 1992. Alteration of nutrition as means to reduce environmental pollution by pigs. *Livestock Production Sciences*, 31: 74-95.

Jongbloed, A.W., Everts, H. and Kemme, P.A. 1991. Phosphorus availability and requirements in pigs. In: W.Haresign and D.J.A. Cole (Editors), *Recent Advances in Animal Nutrition*. Butterworths, London.

Kay, R.M. and Lee, P.A. 1997. Ammonia emission from pig buildings and characteristics of slurry produced by pigs offered low crude protein diets. In: *Proceedings of the International Symposium on Ammonia and Odour Control from Animal Production Facility*. Vinkeloord, The Netherlands, 253-260.

Lau, A.K., Vizcarra, A.T., Lo, K.V. and Luymes, J. 1996. Recirculation of filtered air in pig barns. *Canadian Agricultural Engineering*, 38: 297-304.

Lavoie, J., Marchand, G. and Gingras, G. 1997. Pit ventilation in pig-housing facilities. *Canadian Agricultural Engineering*, 39: 317-326.

Lee, P.A., and Kay, R.M. 1997. Economic implications of reduced crude protein diets for pigs to reduce ammonia emissions. In: *Proceedings of the International Symposium on Ammonia and Odour Control from Animal Production Facility*. Vinkeloord, The Netherlands, 699-706.

Massé, D.I., Droste, R.L., Kennedy, K.J., Patni, N.K. and Munroe, J.A. 1997. Potential for the psychrophilic anaerobic treatment of swine manure using a sequencing batch reactor. *Canadian Agricultural Engineering*, 30: 25-33.

Morken, J. and Sakshaug, S. 1997. New injection technique - Direct Ground Injection (DGI®). In: *Proceedings of the International Symposium on Ammonia and Odour Control from Animal Production Facility*. Vinkeloord, The Netherlands, 585-590.

Mumpton, F.A. and Fishman, P.H. 1977. The application of natural zeolite in animal science and aquaculture. *Journal of Animal Science*, 45(5): 1188-1202.

O'Neill, D.H. and Phillips, V.R. 1991. A review of the control of odour nuisance from livestock buildings: Part 1, Influence of the techniques for managing waste within the building. *Journal of Agricultural Engineering Research*, 50: 1-10.

O'Neill, D.H., Stewart, W.I. and Phillips, V.R. 1992a. A review of the control of odor nuisance from livestock buildings: Part 2, The cost of odour abatement systems as predicted from ventilation requirements. *Journal of Agricultural Engineering Research*, 53: 23-50.

O'Neill, D.H. and Phillips, V.R. 1992b. A review of the control of odor nuisance from livestock buildings: Part 3, Properties of the odorous substances which have been identified in livestock wastes or in the air around them. *Journal of Agricultural Engineering Research*, 53: 23-50.

Perkins, S.L. and Feddes, J.J.R. 1996. The effect of timing of floor application of mineral oil on dust concentrations in a swine farrowing unit. *Canadian Agricultural Engineering*, 38: 123-127.

Prairie Swine Center, 1997. Manure lagoon cover offers odour relief. Canada-Saskatchewan Agriculture, Green Plan Agreement, Feature Articles. Internet document published by the Prairie Swine Center, Canada.

Reynolds, S.J., Donham, K.J., Whitten, P., Merchand, J.A., Burmeister, L.F. and Pependorf, W.J. 1996. Longitudinal evaluation of dose-response relationships for environmental exposures and pulmonary function in swine producer workers. *American Journal of Industrial Medicine*, 29: 33-40.

Ritter, W. F. 1989. Odor control of livestock wastes : State-of-the-art in North America. *Journal of Agricultural Engineering Research*, 42: 51-62.

Rodd, V. 1998. The smell of manure. Nappan Research Farm, Nappan, Nova Scotia. Internet document published by the Nappan Research Farm, Canada.

RQMT. 1994. Règlement sur la qualité du milieu du travail. S-2.1, r.15. Éditeur officiel du Québec, Québec, Canada.

Seedorf, J. 1997. Human health and dust related endotoxin concentrations in livestock buildings. In: *Proceedings of the International Symposium on Ammonia and Odour Control from Animal Production Facility*. Vinkeloord, The Netherlands, 733-740.

Sersale, R. 1983. Zeolite naturali e loro utilizzazioni. *La chimica e l'industria*, 65(12): 764-767.

Siemers, V. and Van den Weghe, H. 1997. Biofilter/wetscrubber combination for the reduction of ammonia, odour and dust emissions of pig fattening houses. In: *Proceedings of the International Symposium on Ammonia and Odour Control from Animal Production Facility*. Vinkeloord, The Netherlands, 537-544.

Sneath, R.W. 1988. Centrifugation for separating piggery slurry 3. Economic effects on aerobic methods of odor control. *Journal of Agricultural Engineering Research*, 39: 199-208.

Sneath, R.W., Burton, C.H. and Williams, A.G. 1992. Continuous aerobic treatment of piggery slurry for odor control scaled up to a farm-size unit. *Journal of Agricultural Engineering Research*, 53: 81-92.

Sutton, A.L., Kephart, K.B., Patterson, J.A., Mumma, R., Kelly, D.T., Bogus, E., Jones, D.D. and Heber, A. 1997. Dietary manipulation to reduce ammonia and odorous compounds in excreta and anaerobic manure storage. In: *Proceedings of the International Symposium on Ammonia and Odour Control from Animal Production Facility*. Vinkeloord, The Netherlands, 245-252.

Swine Odor Task Force. 1995. Option for managing odor. Report from the North Carolina Swine Odor Task Force. Agricultural Research Service, North Carolina State University. (Internet document, 47 pp).

Takai, H., Møller, F., Iversen, M., Jorsal, S.E. and Bille-Hasen, V. 1993. Dust control in swine buildings by spraying of rapeseed oil. In: *International Livestock Environment Symposium*, St-Joseph, MI, USA: ASAE. 726-733.

Williams, P.E.V. and Kelly, J.M. 1994. Animal production and pollution problems. In: Livestock Production for 21st Century. Priorities and research needs ed. P.A. Thacker. University of Saskatchewan Press, Saskatoon, Canada, 159-186.

Young, J.S., Classen, J.J., Bottcher, R.W. and Westerman, P.W. 1997. Biofiltration system for testing the reduction of odor from swine buildings. In: Proceedings of the International Symposium on Ammonia and Odour Control from Animal Production Facility. Vinkeloord, The Netherlands, 521-528.

Zhang, Y., Nijssen, L., Barber, E.M., Feddes, J.J.R. and Sheridan, M. 1994. Applying mineral oil to reduce dust in swine buildings. Transactions of ASHRAE, 100(2): 1043-1050.

Zhu, J., Bundy, D.S., Li, X. and Rashid, N. 1997. A procedure and its application in evaluating pit additives for odor control. Canadian Agricultural Engineering, 39: 207-214.

CONNECTING STATEMENT

In order to find an economically viable and promising solution to the environmental problems facing the swine industry, zeolite has been tested as a mineral supplement improving the productivity of the animals. Zeolite has the ability to trap ammonia inside the intestinal tract and to increase feed efficiency. A reduction of the environmental impact is thus expected. Hence, the next chapter tests the effects of zeolite as a mineral supplement on swine growth performance and piggery air quality. The fourth chapter describes a versatile dynamic olfactometer conceived and built to analyze the effects of zeolite on odors emanating from the experimental rooms. The olfactometer construction was not completed at the time of the zeolite trial. Therefore, effects of zeolite on piggery odor levels were tested subjectively with the use of panelists standing directly in the rooms.

Chapter three deals with the zeolite test. Zeolite was used in the ration of growing and finishing pigs at levels of 2 and 5%. The effect on pig's growth performance and air quality were tested and compared. Trials have demonstrated that it is possible to decrease the feed gain ratio by 0.14 to 0.19 kg of feed per kg of body weight gain with the use of 2% zeolite for pigs of 25 to 40 kg and 5% zeolite for pigs of 40 to 100 kg when compared to pigs receiving a ration with the same level of energy and protein.

This paper will be submitted for publication in **Journal of Bioresource Technology**. **Authors: Choinière, D., Barrington, S.F. and Downey, B.** The contribution of the authors are: i) First author carried out entire experimental work with the zeolite: collected the data, analyzed the statistics and collaborated in the writing of the article ii) Second author supervised the research and co-edited the article iii) Third author gave scientific advice on the pig's nutrition and helped correct the article.

CHAPTER III

Zeolite as a Mineral Supplement to Improve Swine Productivity and Piggery Air Quality

3.1 Abstract

The development of the swine industry is constrained by the environmental impact of its manure, on water, soil and air. Fed as a mineral supplement, zeolite can help reduce this impact while improving the productivity of the operation. Clinoptilolite is the preferred zeolite because of its ability to adsorb water and specifically NH_4^+ in the intestine. Thus, it can slow down the passage of feed and improve the intestinal absorption of ammonium. Zeolite (77% clinoptilolite) was fed as a mineral supplement to a group of hogs in a specific room and their growth performance (feed conversion ratio, rate of weight gain, feed intake and carcass quality) was compared to another group of hogs of equivalent gender and initial weight, housed in a similar adjoining room receiving the control feed. The control feed contained fine silica sand instead of zeolite. Two levels of zeolite were tested, 2 and 5%. The ambient air CO_2 , NH_3 and H_2S levels were monitored every week in both the control and zeolite room. The zeolite significantly improved the feed conversion rate and reduced the feed intake when supplemented at a level of 2% to hogs weighing less than 40 kg. When the hogs weighed more than 50 kg, a 5% level significantly improved the feed conversion ratio and reduced the feed intake. There was no significant difference in ambient air NH_3 level between the zeolite and control room, but diluting the feed from 2 to 5% sand or zeolite reduced the ambient level from 12.5 to 8.7 ppm, respectively. The ventilation rate was the only factor found to affect CO_2 levels and no significant amount of H_2S was detected. Some 15 panelists directly evaluated the air of the two rooms to find that the zeolite room had a slightly lower odour level.

3.2 Introduction

Agriculture is an important economic sector for Canada. In close competition with those of cash crops and milk, swine enterprises gross \$3 billion annually. Furthermore, the Canadian agri-food industry has experienced in recent years, an excellent annual growth of 4.6% and employs 12% of the Canadian work force (Statistics Canada, 1997). Among all agricultural sectors, the swine industry is the most promising, with several provinces planning to expand their output by 20 to 100% within the next 5 years. However, this growth program has been constrained by many communities concerned about air, soil and water pollution.

Fed as a mineral supplement, zeolite can reduce the environmental impact of the swine industry by improving nutrient absorption in the gut of the hogs, reducing the manure nutrient content and lowering the incidence of soil and water pollution. By reducing the ammonia content of manure, zeolite can lower its N volatilization.

3.3 Literature Review

Zeolite, a tectosilicate, is a volcanic mineral with a crystalline hydrated aluminosilicate structure containing positively charged metallic ions of the alkali and alkaline earth elements (Pecover, 1987). The crystals are characterized by SiO_4 tetrahedra where all four corner oxygen ions are shared with adjacent tetrahedra to form a three-dimensional framework. Because some silicon atoms are replaced by trivalent aluminum atoms, a deficiency in positive charges arises. Thus, zeolite possesses a cation exchange capacity (CEC) reaching in some instances 500 meq/100g as compared to Montmorillonite with a CEC of 80 to 100 meq/100g (Mumpton and Fishman, 1977). As compared to other tectosilicates, such as feldspar and quartz, zeolite possesses a remarkably open framework where void spaces can occupy up to 50% of the total volume (Airoldi *et al.* 1993). There exist approximately 45 types of zeolite with varying cavity size (molecular sieving capacity) and some zeolites, such as chabasite, phillipsite and clinoptilolite, are known to selectively adsorb NH_4^+ (Sersale, 1983).

Sodium zeolite A (SZA) and clinoptilodite have been used as a mineral feed supplement because of their respective abilities to adsorb Ca_2^+ and NH_4^+ along with water. Their respective CECs are of the order of 500 and 120 meq/100g. SZA has been produced synthetically with a CEC of 700 meq/100g. While SZA contains mostly exchangeable Na (12.5%), clinoptilolite offers Ca and K at levels of 1.5 and 2.5%, respectively. SZA has the highest affinity for Ca and has been used to improve the adsorption of Ca and for ion exchange to reduce the toxicity of excess salts, especially in poultry feed (Fethiere *et al.*, 1994; Rolland *et al.*, 1985). Using in vitro tests, Holthaus *et al.* (1996) demonstrated that SZA can replace sodium bicarbonate to improve the digestibility of feed, without any negative effect on rumen function. Compared to a control diet, synthetic SZA at a level of 2% was found to have a negative effect on the digestibility of dairy cattle feed (Johnson *et al.*, 1988), whereas 2% natural SZA had no effect. In chicks, SZA was able to exacerbate the adverse effects of excess dietary Ca (Watkins *et al.*, 1989).

Clinoptilolite has a special affinity for NH_4^+ and has thus been used to improve nitrogen absorption in feed. The difference in affinity between SZA and clinoptilolite is due to the size of the openings between their lattice work. Since clinoptilolite has the most potential for improving the growth of livestock while improving N absorption and reducing NH_3 volatilization, it will be further examined.

Added to feed at the level of 5%, clinoptilolite has improved the growth rate of domestic animals and reduced manure NH_3 and odor emissions (Bartko *et al.*, 1993). Ma *et al.* (1979) reported an increase in litter size of 1.78 piglets when feeding clinoptilolite at levels of 5% to pregnant Landrace sows. However, in a second test with 5% clinoptilolite, Ma *et al.* (1983) did not observe any significant effect on embryo survival and total ovarian weight, 24 days after inseminating sows. Airoidi *et al.* (1993) reported the wide use of zeolite by Italian farmers to reduce odor emission and improve feed conversion of grower hogs. However, they failed to measure any significant decrease in NH_3 .

levels and improvement in hog growth when feeding 5% zeolite (55% phillipsite, 15% chabasite, 15% bentonite and 15% illite) with a CEC of 265 meq 100g⁻¹. Vrzgula and Bartko (1983) obtained an increase in weight gain of 0.49 kg/week with hogs fed a 5% clinoptilolite ration as compared to those fed a regular ration. Also, the pigs fed clinoptilolite produced less odoriferous feces and those with diarrhea produced firmer feces within 24 hours of testing. Barrington and El Moueddeb (1995) demonstrated that 5% zeolite (77% clinoptilolite) in swine feed improved feed conversion by 0.15 kg of feed per kg of body weight gain. It also improved carcass quality by \$0.05/kg and reduced manure NH₃ volatilization during the summer.

In Cuba, weaning pigs at 33 days of age with an average body weight of 6 kg were tested with different levels of clinoptilolite in a wheat/corn/fish diet. The best performance was obtained with 3% zeolite. An improved weight gain and feed efficiency were recorded as compared to pigs on a control diet containing no zeolite (Castro and Pastrana, 1980). An improved feed conversion was also obtained with the addition of 5% clinoptilolite in a typical Cuban diet for growing pigs from 35 to 65 kg. This feed contained 64% molasses. With zeolite, average daily gain was improved by 13% and the stool samples of pigs held less water than those of the control group (Castro and Elias, 1980). During the finishing phase, from 65 to 100 kg of body weight, the best response was obtained with 7.5% clinoptilolite in the diet.

When used in adequate levels, clinoptilolite has a significant effect on the adsorption of minerals and water in the digestive tract of animals, without altering the quality of the meat or product. Nestorov (1981) demonstrated that clinoptilolite in the rumen adsorbs the free NH₄⁺, helps reduce its toxic effect, improves NH₄⁺ ingestion by cattle and improves growth efficiency. In ruminants, protein hydrolysis alone does not suffice in providing NH₄⁺ to microbes while urea supplements generally produce excessive amounts of NH₄⁺, the urease enzyme being plentiful in the rumen. Thus, clinoptilolite in the presence of urea, acts as a buffer, adsorbing the excess NH₄⁺ but releasing it for the microbes

of the rumen and later in the small intestine. Tsitsishvili (1978) demonstrated that clinoptilolite had no effect on blood analysis when fed as a mineral supplement and improved crude protein and free N digestibility from 73 to 76% and 89 to 94%, respectively for grower hogs.

The CEC and level of zeolite used directly affect the performance of the animals because too strong an adsorption effect hinders nutrient ingestion. Clinoptilolite with a CEC of 100 to 140 meq/100g and feed at levels ranging between 2 and 7.5% generally improves cattle and hog performance. When less than 1% is fed, clinoptilolite and natural SZA have no effects (Ward *et al.*, 1991). Synthetic SZA with a much higher CEC negatively affects growth, compared to the same level of natural SZA which offers approximately half the CEC (Elliott *et al.*, 1991).

3.4 Objective

The objective of this research project was to investigate the performance of grower hogs (25 to 100 kg) fed a ration supplemented with 2 and 5% zeolite (77% clinoptilolite). Animal performance was measured by monitoring the rate of feed conversion, weight gain and feed consumption and by measuring carcass quality. The performance of the grower hogs fed the zeolite ration was compared against a comparable control group fed with a ration supplemented with fine silica sand at the same level as zeolite. The purpose of adding sand in the control feed is to obtain two similar rations in terms of protein, energy and fiber content. Having similar rations allows to test the effects of zeolite without testing the effects of reducing the protein, energy and fiber content due to the addition of zeolite. Room air CO₂, NH₃ and H₂S levels were also monitored and compared, to insure comparable conditions among experimental rooms. Furthermore, NH₃ monitoring provided information on the effect of zeolite on ambient air conditions.

3.5 Materials and Methods

3.5.1 The Experimental Piggery

The study was conducted at the experimental swine unit on the Macdonald Campus of McGill University, Ste-Anne-de-Bellevue (Montreal, Quebec) during the winter of 1997/98. This complex houses 50 sows in a farrow to finish operation.

The experiment used the two identical grower rooms measuring 14.75 m by 7.60 m, with a ceiling height of 3.05 m. Each room has a central walkway measuring 1.60 m in width with 8 pens on each side, each of 3.00 m by 1.84 m. The animals are housed at a density of six hogs per pen or 0.766 m²/hog. Each room is ventilated by three fans, 300 mm, 400 mm and 600 mm in diameter, which are controlled by a common thermostat. The air inlet in each room consists of four pairs of ceiling panels, 0.9 m in length, opened against a counter weight by the room negative pressure. A recirculating duct under these slots keeps the ambient and fresh air in suspension (Agriculture Canada, 1992). The ventilation system produces a ventilation rate of 20.0 and 48.0 l/s/hog with two and three fans in operation, respectively. The pen floors are fully slatted and all pigs are fed ad libitum from standard upright feeders located at the front of the pens.

All hogs were weighed using an Alley WeighTM electronic scale with a capacity of 1 000 kg, an accuracy of ± 0.5 kg (Alley WeighTM by Weigh-Tronix, Fairmont, MN). The scale indicator was a Tronix Model 615 (Weigh-Tronix, Fairmont, MN). The CO₂, NH₃ and H₂S levels in the experimental rooms were measured using a Multiwarn II System (Dräger, Moislinger Allee, Germany). This system had an infra-red radiation probe to measure the CO₂ levels and electro-chemical sensors to measure NH₃ and H₂S levels. The probes were calibrated with standard gas concentrations, in the range of 1 and 50 ppm. The probe's accuracy was equivalent to 5% of the reading.

During the two phases of the experiment (November-December 1997 and February-April 1998), pigs in grower room #2 were fed a ration supplemented with zeolite while those in grower room #1 were given the control feed. The manure of both experimental rooms was

removed by gutter scrappers and dumped into a gravity flow gutter in the hall way just outside both rooms. This gravity flow gutter leads the manure into a prepit. Although grower room #1 was located closer to the manure prepit, gas traps installed at the room gutter outlets prevented the return of prepit gases.

3.5.2 Experimental Material

The experimental zeolite contained 77% clinoptilolite and was provided by Nutrimin Inc. It had a CEC of 130 meq/100g and a particle size mostly under 500 μm (Table 3.1).

Table 3.1: Characteristics of the experimental zeolite

Property	Unit	Value
Physical Properties		
Specific gravity		0.95
Bulk density	kg/m^3	813
Hardness		3.5
Melting point	$^{\circ}\text{C}$	1 380
Dry brightness		66
pH stability		2.5-12
Channel dimension	\AA°	3.9 to 5.4
Particle size		
< 10 μm	%	34
10-100 μm	%	6
100-500 μm	%	44
500-700 μm	%	16
Chemical Properties		
pH		7.2
CEC	meq/100g	130
Exchangeable cations		
Ca	meq/100g	30.0
Mg	meq/100g	0.63
K	meq/100g	67.5
Na	meq/100g	30.0

Table 3.1: Characteristics of the experimental zeolite (cont.)

Property	Unit	Value
Zeolite Content		
Clinoptilolite	%	77
Siderite	%	8
Quartz	%	5
Plagioclase	%	3
K-Feldspar	%	2
Barite	%	3
Magnetite	%	2
Total	%	100
Mineral Content		
Aluminum	g/kg	30.5
Barium	mg/kg	730
Cadmium	mg/kg	<0.025
Copper	mg/kg	248
Magnesium	mg/kg	4358
Lead	mg/kg	24.3
Selenium	mg/kg	<0.025
Mercury	mg/kg	0.018
Potassium	mg/kg	6763
Ammonium	mg/kg	14.8
Sodium	mg/kg	1056
Lithium	mg/kg	3.05
Silver	mg/kg	<0.350
Arsenic	mg/kg	<1.00
Zinc	mg/kg	31.8
Cobalt	mg/kg	<3.00
Nickel	mg/kg	2.40
Chromium	mg/kg	5.35
Thallium	mg/kg	0.006
Oxides		
Calcium	mg/kg	5328
Magnesium	mg/kg	2623
Sodium	mg/kg	1183
Potassium	mg/kg	9480
Aluminum	mg/kg	4207
Iron	mg/kg	14 529
Manganese	mg/kg	481
Titanium	mg/kg	472
Silicon	mg/kg	506

Twice a month, the experimental feed was manufactured by the Coopérative Fédérée Mill, Ste-Rosalie, Quebec. It consisted of a standard swine ration of soybeans and corn, with 16% crude protein (Table 3.2). The zeolite and control feed were supplemented, respectively, with zeolite and fine silica sand. During the experiment (November to December 1997 and February to April 1998), the energy and crude protein levels of the feed were not corrected after the addition of sand or zeolite.

Table 3.2: Characteristics of the swine ration

Property	Unit	Value
Crude protein	% min.	16
Crude fat	% min.	2.5
Crude fiber	% max.	5
Calcium	%	0.75
Phosphorus	%	0.57
Sodium	%	0.20
Zinc	mg/kg	140
Copper	mg/kg	103
Selenium	mg/kg	0.3
Vitamin A	iu/kg	9.525
Vitamin D-3	iu/kg	890
Vitamin E	iu/kg	26

The grower hogs used for the experiment were 75 % Landrace x 25% Yorkshire cross bred. They were raised in a weaning room up to a weight of 20 kg and then transferred into the grower room for the experiment. During their last week in the weaning room, they were weighed and randomly assigned to one of the two groups of equal weight and sex distribution. Immediately upon being transferred to the grower room, the hogs were placed on the zeolite or control feed.

3.5.3 Methodology

The nutritional benefits of zeolite as a mineral supplement in the

diets of pigs was evaluated during the complete growth period of the two equal groups (same average weight, same number of male and female) of around 80 hogs finished during each two phases, from weaning to 105 kg live weight. This represented the conditions prevailing in a typical commercial grower hog operation. Nevertheless, only the results of 120 hogs and 108 hogs in first and second phase respectively has been used for the statistical analysis since some pigs were sent to the market during the experiment.

The experiment was split into two phases. During the first phase (November-December 1997), feed containing 2% of zeolite was fed to the zeolite groups of pigs while feed containing 2% of sand was fed to the control group of pigs. During the second phase, (February-April 1998), the level of zeolite and sand was of 5% instead of 2%. Winter conditions prevailed during the two phases, except for the last week of the second phase where summer conditions prevailed for exterior temperatures reached 24°C during the day.

Animals were added to and removed from each experimental room on a continual basis, rather than on an "all in all out" basis. On a regular basis, groups of 40 to 50 weaned pigs were weighed, identified and split into two groups of identical weight and sex. One group was transferred into one grower room and fed a standard swine ration with zeolite while the other group was transferred to the other identical grower room and fed the standard ration with sand. In each room, the weaned pigs were further split into subgroups of 6 pigs and each subgroup was placed in a single pen. Each pig was identified by ear notching and its pen number was recorded. Feed consumption and feed conversion rate were averaged for all six hogs in each pen while weight gain was calculated for each individual pig.

Following a one week period of acclimatization to their environment, the experimental animals were weighed a second time and officially placed on test. Feed was weighed and added to the individual feeders once every two days. The animals were weighed every two

weeks, at which time the feeders from each pen were weighed to calculate the feed conversion rate. The hogs were sent to the market at a weight of 100 to 110 kg. Each animal was identified by a tattoo before being sent to the slaughterhouse. The slaughterhouse could record, for each experimental hog their carcass weight and index. Quebec hog producers are paid according to the carcass index which is determined by the carcass quality. Amongst the different factors considered to determine the carcass index is the carcass weight, length, color of the meat and quantity of fat.

The temperature inside and outside both test rooms was noted electronically every minutes and these records were used to adjust the thermostats for an even ventilation in both experimental rooms. Every weeks, NH_3 , CO_2 and H_2S levels in both rooms were measured every minute over a 24 hour period using the Dräger Multiwarn II System. The measurements were carried out in the center walkway of the rooms, at two thirds of the length towards the fans, and at a height of 1,2m.

Odor evaluations were conducted once during the first stage of the experiment and once during the second stage of the experiment. Each time, a total of 15 panelists were asked to stand in each room, and evaluate the odor level subjectively. The evaluation was conducted in one room and then in the other. The test took no more than 15 minutes. They were asked to rate the odor level using a scale of 1 to 5 where 1 represents a very unpronounced odor, 2 an unpronounced odor, 3 a pronounced odor, 4 a very pronounced odor, 5 a very very pronounced odor.

3.5.4 Statistical Analysis

A temporal repeated-measures ANOVA with a randomized complete block design was used in this experiment to observe the variation in average daily feed intake (ADI), average daily weight gain (ADG) and feed to gain ratio (F/G). The experimental design was composed of four blocks with two to four replicates per block, two treatments (Control and Zeolite), four repeated-measures and one

covariable. The use of a covariable was necessary in this experiment to take into account the differences in weight between groups of pigs. The covariable corresponds to the initial weight of pigs at the beginning of each test phase. In this experiment, time was the repeated factor (von Eden, 1993). This statistical model represents fairly the trial executed, but presents some draw backs. Firstly, the effects of the covariable are too strong: they overcome the expected time effect. Consequently, this model has been compared with two other similar statistical models (1- same model described above but without covariable, 2 - same model as no. 1 but dividing every ADG, ADI and F/G by the covariable) and similar significant results are obtained. Secondly, the model does not measure the direct effect of the treatment versus the pig's weight. Thus by splitting the data into two groups (pigs below 60 kg and pigs above 60 kg) it's possible to partially overcome this disadvantage. (See appendix A to D)

The carcass indexes were compared using an AOV procedure where treatments (zeolite or sand) and block (carcass weight) effects were compared (Steel and Torrie, 1986).

3.6 Results and Discussion

3.6.1 Animal Performance

The performance of the hogs (ADG, AFI and F/G) is compared for the two phases of the experiment in Figures 3.1 and 3.2. During the first phase of the experiment (Figures 3.1), using 2% zeolite or sand, the zeolite had a significant effect on F/G and AFI for hogs weighing less than 40 kg. For the hogs weighing 20 kg, the 2% zeolite feed decreased the F/G ratio by 0.14 kg, reduced the ADI by 0.1 kg of feed, but had little effect on the ADG. For the hogs weighing more than 40 kg, the zeolite supplement had no significant effect. For those hogs weighing more than 60 kg, the zeolite feed had a slightly depressing effect on the F/G and the ADI with little effect on the ADG.

Adding zeolite at a low level, to the diet of large animals, had a

negative effect on their feed to gain ratio (Figure 3.1). This can be explained from the fact that the energy and protein level of the experimental feed had not been adjusted for the additive, and that the test was started using animals of variable weight. When 2% zeolite or sand feed was given to hogs, all sizes of animals received the feed. Thus, the larger animals (over 60 kg) were switched from a regular to a lower energy feed, unadjusted for the additives, and showed slight negative effects.

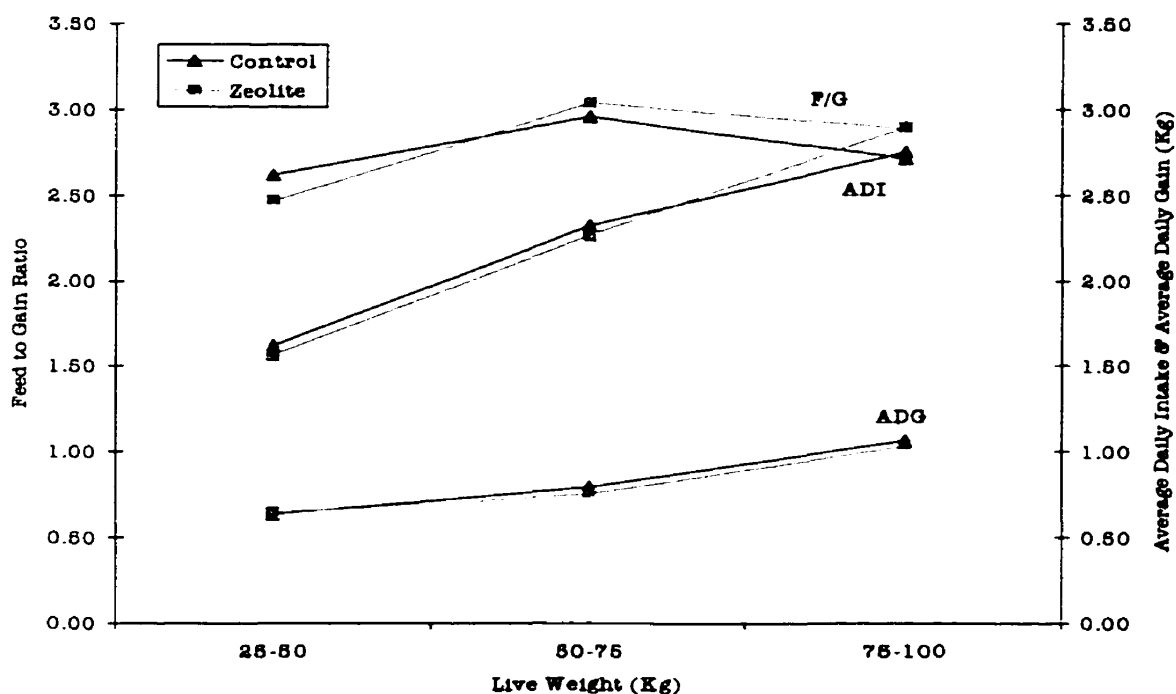


Figure 3.1 The F/G (Feed to Gain ratio), ADI (Average Daily feed Intake) and ADG (Average Daily Gain) versus weight with the feed containing 2% zeolite and 2% sand (control) (Phase 1).

For the second phase of the experiment (Figure 3.2), the 5% zeolite feed had a significant effect on the hogs weighing over 40 kg. For those hogs weighing 75 to 100 kg, the F/G ratio was reduced by 0.19 kg of feed per kg of body weight gain. The ADI was reduced by 0.4 kg while the ADG was not affected significantly.

The fact that ADI and F/G, but not the ADG, were affected by the

zeolite indicates that zeolite may indeed slow down the passage of feed through the intestine of the pigs. Zeolite could indirectly slow down the passage of feed by absorbing water in the intestine and reducing the ADI of feed without affecting growth rate, thereby improving feed efficiency (Figure 3.2).

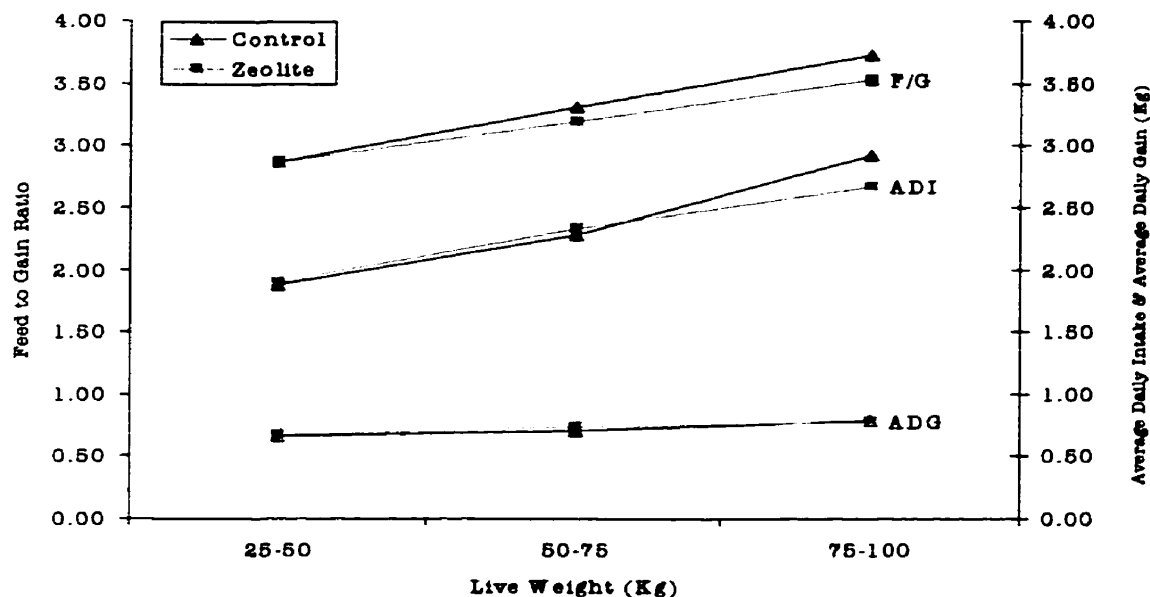


Figure 3.2 The F/G (Feed to Gain ratio), ADI (Average Daily feed Intake) and ADG (Average Daily Gain) versus weight with the feed containing 5% zeolite and 5% sand (control)(Phase 2).

From this experiment, the benefits of zeolite can be expressed in terms of a reduction of feed consumption per finished pig. If a F/G decreases by 0.14 for hogs of 25 to 40 kg by using 2% zeolite and F/G decreases by 0.19 for hogs of 40 to 100 kg by using 5% zeolite, this represents a feed economy of 13.5 kg per finished hog.

Data from the first and second phase show that the energy and protein level of the feed has an effect on the feed to gain ratio. Hogs of 50 kg fed a ration diluted with 2% zeolite had a F/G of 3.0 while with the 5% treatment, the F/G was over 3.2.

The carcass quality of all hogs fed zeolite and sand is reported as a function of carcass weight for all experimental hogs (Figure 3.3). Zeolite tended to improve carcass quality of all hogs with carcasses weighing under 85 kg although the difference was not significant due to the high standard deviation. The same results were observed by Barrington and El Moueddeb (1998). To better measure the effects of zeolite on carcass quality, the experiment needs to be repeated using 2% zeolite when the hogs weigh less than 40 kg, and 5% zeolite when the hogs weigh over 40 kg and this must be done on an "all in all out" basis.

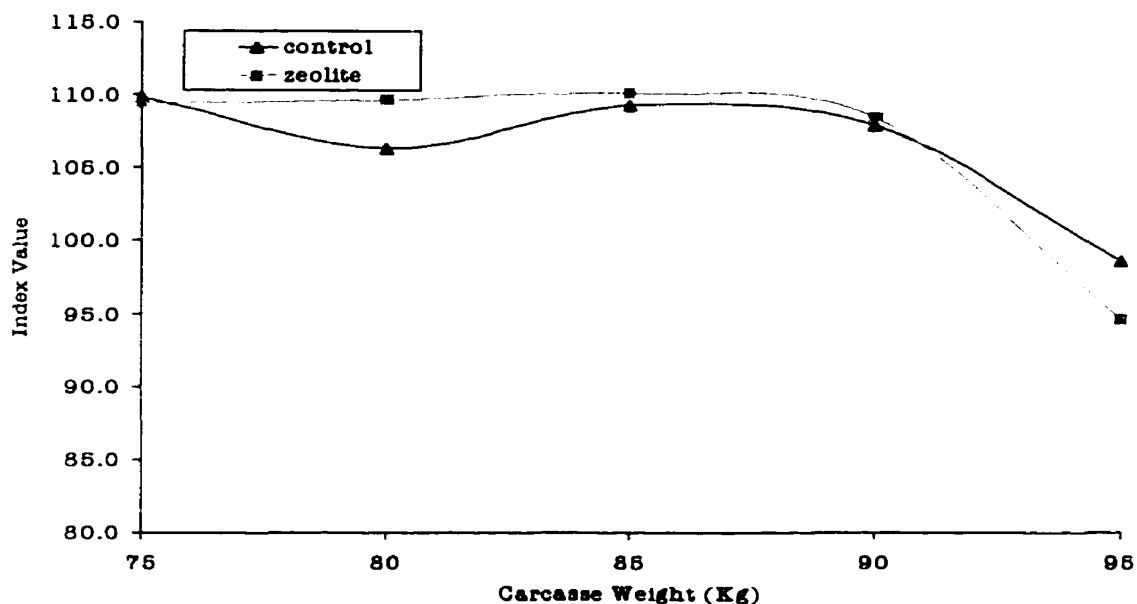


Figure 3.3 The over all carcass index versus carcass weight for hogs fed the zeolite and sand (control feed).

During the test period, no specific health problems were observed, except for some tail biting when the hogs were initially transferred into the grower room. Tail biting was more evident during the last week of the second phase of the experiment when outside conditions changed rapidly from winter to summer.

3.6.2 Ambient Air Quality

The levels of ammonia, carbon dioxide and hydrogen sulphide are reported in Table 3.3 for each phase of the experiment. The zeolite feed

had no significant effect on the levels of all three gases, but the dilution level of the supplement (zeolite or sand) and the ventilation rate had a significant effect.

Table 3.3: Air quality in the experimental rooms

Trial	Carbon dioxide (% by volume)		Ammonia (ppm)		Hydrogen sulphide (ppm)	
	Control	Zeolite	Control	Zeolite	Control	Zeolite
2% zeolite Nov-Dec 97 Phase 1 Winter vent.	0.21 (.060)*	0.19 (.040)	12.29 (2.881)	12.63 (2.256)	<0.001	<0.001
5% zeolite Feb-Apr 98 Phase 2 Winter vent.	0.16 (.029)	0.17 (.037)	7.38 (3.566)	9.18 (3.049)	0.005 (.032)	0.004 (.024)
5% zeolite Feb-Apr 98 Phase 2 Sum vent.	0.08 (.009)	0.08 (.010)	3.65 (1.299)	4.21 (1.567)	<0.001	<0.001

* The values in parenthesis are the standard deviation.

At the beginning of the experiment, both experimental rooms had an ammonia level of 50 ppm. This level dropped with the installation of gas traps inside the manure gutters at their outlet into the main gutter leading to the prepit. With these gas traps in place, the ambient ammonia level dropped to 12 ppm with the 2% zeolite or sand feed. Nevertheless, the ambient ammonia level was lowered to an average level of 8.7 ppm when feeding 5% zeolite or sand. Thus, the feed diluted with the 5% supplement had a lower N content, than that with the 2% supplement, and this had a positive effect on manure N volatilization. Also, this drop can partially be attributed to the slightly higher ventilation rate during the second phase of the experiment, as opposed

to the first phase (Table 3.4). During the last week of the second phase of the experiment, the ammonia levels dropped to 3 to 4 ppm, as the ventilation rate was drastically increased. Thus, the management of the ventilation system and the level of crude protein in the feed had a more significant effect on the ambient ammonia levels than the zeolite supplement in the feed.

Table 3.4: Air temperature and ventilation in the experimental rooms

Trial	Average Temperature		Fan Operation (% of the time)					
	°C		300mm fan		450mm fan		600mm fan	
	Control	Zeolite	Control	Zeolite	Control	Zeolite	Control	Zeolite
2% zeolite Nov-Dec 97 Phase 1 Winter vent.	16 (.408)*	16 (.321)	92	92	31	30	0	0
5% zeolite Feb-Apr 98 Phase 2 Winter vent.	18 (.634)	18 (.392)	95	96	49	45	0	0
5% zeolite Feb-Apr 98 Phase 2 Sum vent.	21 (2.94)	21 (2.37)	99	99	91	93	48	46

* The values in parenthesis are the standard deviation.

The high value of the standard deviation for the NH_3 can be explained by the fact that it has been calculated from several 24 hour period data and that the NH_3 level tends to be 3 to 4 ppm higher on average during the day then during the night. Furthermore, the NH_3 can quickly increase by 3 to 5 ppm as soon as someone enters the room.

It takes approximately 45 to 60 min for this level to return to normal.

The CO₂ level was lower during the second phase of the experiment because of the slightly higher ventilation rate (Table 3.4). During the last week of the second experimental phase, it dropped to 0.08 % by volume, with the summer ventilation rate. Very limited H₂S levels were detected only during the second phase of the experiment.

Although the difference was not significant, the zeolite room had a slightly higher NH₃ and CO₂ level than that of the control room. This can be attributed to the slightly higher ventilation rate in the control room, especially for the 450mm fan (Table 3.4).

Table 3.5: Subjective room air odor evaluation

Trial	Odor Rating (1-5)	
	Control	Zeolite
2% zeolite Nov-Dec 97 Phase 1 Winter vent.	3.05 (.844)*	2.10 (.526)
5% zeolite Feb-Apr 98 Phase 2 Winter vent.	3.16 (1.006)	3.16 (0.856)

Note: the intensity of the odor rating increases from 1 to 5.

* The values in parenthesis are the standard deviation.

During the first and second phases of the experiment, the level of odor in both rooms was evaluated subjectively. The 15 panelists evaluated the odor level as slightly lower in the zeolite room during the first phase and equal during the second phase of the experiment (Table 3.5). This may have resulted from the slightly higher ventilation rate persisting in the control room during the second phase of the experiment (Table 3.4). Again, ventilation management and room

cleaning practices may have had a more significant effect on odor level than zeolite.

3.7 Conclusions

Zeolite supplement in the ration of grower hogs improved feed efficiency when compared to feed having the same energy and crude protein levels. For hogs weighing less than 40 kg, zeolite at a level of 2% reduced the feed required per kg of gain while 5% zeolite was required to produce some effect for hogs over 40 kg. Thus, the use of zeolite at a rate increasing from 2 to 5%, with the weight of the hogs, could reduce feed consumption by 13.5 kg/finished hog. This represents a 5.8% reduction in feed consumption and probably a similar reduction in manure production. Consequently, this reduces the environmental impact of the swine production.

As compared to the control feed containing an equivalent amount of sand, zeolite had no significant effect on the ammonia level of the ambient air in the experimental rooms. But, the dilution of the feed with 2 and 5% zeolite or sand reduced the amount of ammonia in the ambient air. Thus, zeolite can reduce the ammonia level by allowing the use of feed with a lower crude protein level. The management and design of the ventilation system, the ventilation rate and the feed crude protein level had a significant effect on the ammonia and carbon dioxide. Panelists found that the odor level in the zeolite room was slightly less during the first phase of the experiment. On a 1 to 5 scale, the zeolite room obtained a grade of 2 (unpronounced odor) while the control room obtained a grade of 3 (pronounced odor). Again, other factors may have had more influence on the odor level than the use of zeolite.

3.8 Acknowledgment

This work was conducted thanks to the financial help of NSERC and the Fédération des Producteurs de Porcs du Québec. The zeolite was supplied by Nutrimin Canada inc. of Calgary, Alberta.

3.9 References

Agriculture Canada. 1992. Ventilation of small livestock. Agriculture Canada, Ottawa, Ontario, Canada.

Airolidi, G., Balsari, P. and Chiabrandio, R. 1993. Odour control in swine houses by the use of natural zeolites: First approach to the problem. In: Livestock Environment IV, Fourth International Symposium, ASAE, St Joseph, Michigan, USA. 701-708.

Al-Kanani, T., Akochi, E., MacKenzie, A.F., Alli, I. and Barrington., S.F. 1992. Odour emission from liquid hog manure: Effect of added amendments and aeration on odour presence and odour offensiveness. Journal of Environ. Quality, 21: 704-708.

Barrington, S.F. and El Moueddeb, K. 1995. Zeolite as swine manure additive to control odours and conserve N. CSAE paper no. 95-510, Saskatoon, Canada.

Bartko, H., Seidel, H. and Kovac, G. 1993. In: Zeolite '93. Fourth International Conference on the Occurrence, Properties and Utilization of Natural Zeolites. International Committee on Natural Zeolites, Department of the Earth Sciences, SUNY-College at Brockport, Brockport, New York 14420, USA, 43-44.

Castro, M. and Pastrana, M. 1980. Natural Zeolites, Report Compañía de Minerales Tecnicos, Comintec S.A., Republica de Cuba.

Castro, M. and Elias, A. 1980. Natural Zeolites. Report Compañía de Minerales Tecnicos, Comintec S.A., Republica de Cuba.

Elliott, M.A. and Edwards, H. M. 1991. Comparison of the effects of synthetic and natural zeolite on laying hens and broiler chicken performance. Poultry Science, 70: 2115-2130.

Fethiere, R., Miles, R.D. and Harms, R.H. 1994. The utilisation of sodium in Na zeolite A by broilers. *Poultry Science*, 73: 118-121.

Holthaus, D.L., Richardson, C.R., Swift, S.M., Gibson, A.S. and Bunger, F.L. 1996. Effect of zeolite materials on rumen fermentation characteristics when compared to sodium carbonate. *Journal of Animal Science*, 74(supplement): 284.

Johnson, M.A., Sweeney, T.F. and Muller, L.D. 1988. Effects of feeding synthetic zeolite A and sodium bicarbonate on milk production nutrient digestion and rate of digest passage in dairy cows. *Journal of Dairy Science*, 71: 946-953.

Ma, C.-S., Yang, S.K., Tzeng, C.-M. and Wu., M.-K. 1983. Effect of feeding clinoptilolite on embryo survival in swine. *International Committee on natural Zeolite*, 151-156.

Ma, C.-S., Tzeng, C.-M., Lai, M.-K. and Tsai, A.-H. 1979. The feeding of zeolite on the litter size at birth of swine. *Science Agriculture*, 33: 203-209.

Mumpton, F.A. and Fishman, P.H. 1977. The application of natural zeolite in animal science and aquiculture. *Journal of Animal Science*, 45(5): 1188-1202.

Nestorov, N. 1984. Experiences with zeolite and animal husbandry in Bulgaria. In: *Zeo agriculture: The use of natural zeolite in agriculture and aquaculture*. Editors: W.G. Pond and F.A. Mumpton. *International Committee on Natural Zeolites*, Brockport, N.Y., USA, 306pp.

Pecover, S.R. 1987. A review of the formation and geology of natural zeolites. In: *Natural zeolite*, New South Wales Geological Survey, Report GS 1987/145, Department of Mineral Resources, Australia.

Pond, W.G. 1984. Response of growing lambs to clinoptilolite or zeolite Na added to corn, corn-fish meal and corn-soybean meal diets. *Journal of Animal Science*, 59: 1320-1327.

Poulsen, H.D. and Oksbjerg, N. 1995. Effects of dietary inclusion of a zeolite (clinoptilolite) on performance and protein metabolism of young growing pigs. *Animal Feeding and Technology*, 53: 297-303.

Roland, D.A., Laurent, S.M. and Orloff, H.D. 1985. Shell quality as influenced by zeolite with high ion-exchange capacity. *Poultry Science*, 64: 1177-1187.

Sersale, R. 1983. Zeolite naturali e loro utilizzazioni. *La chimica e l'industria*, 65(12): 764-767.

Shurson, P.K., Miller, E.R. and Yokoyama, M.T. 1984. Effects of zeolite A or clinoptilolite in diets of growing swine. *Journal of Animal Science*, 6: 1536-1545.

Statistics Canada. 1996. *Agricultural Financial Statistics*, Catalog no. 21-205-XPB. Statistic Canada, Ottawa, Canada.

Steel, R.G.D. and Torrie, J.H. 1986. *Principles and procedures of statistical analysis. A biometrical approach*. McGraw Hill Publishing Corporation, New York, U.S.A.

Tsitsishvili, G.V. 1978. Adsorption and catalytic properties of some soviet natural zeolites: In *Natural Zeolites: Occurrence, Properties, Use*. L.B. Sand and F.A. Mumpton eds., Pergamon Press, Elmsford, New York, USA, 397-401.

Vissek, W.J. 1978. The mode of growth promotion by antibiotics. *Journal of Animal Science*, 46: 1447.

Von Ende, C.N. 1993. Repeated-measure analysis. Growth and other time dependent measures. In: Design and Analysis of Ecological Experiments. Scheiner S.M. and J. Gurevitch, Editors, Chapman and Hall, New York, USA, 113-137.

Vrzgula, L. and Bartko, P. 1983. Effects of clinoptilolite on weight gain and some physiological parameters of swine. International Committee on natural Zeolite, 157-162.

Ward, T.L., Watkins, K.L., Southern, L.L., Hoyt, P.G. and French., D.D. 1991. Interactive effects of SZA and Cu in growing swine: growth and bone and tissue mineral concentrations. Journal of Animal Science, 69: 726-733.

Watkins, K.L., Vagnoni, D.B. and Southern, L.L. 1989. Effect of dietary SZA and excess Ca on growth and tibia Ca and P concentration in uninfected and Eimeria acervulina-infected chicks. Poultry Science, 68: 1236-1240.

Watkins, K.L. and Southern. L.L. 1991. Effect of dietary Na zeolite A and graded levels of Ca on growth, plasma and tibia characteristics of chicks. Poultry Science, 70: 2295-2303.

CONNECTING STATEMENT

In order to measure odors emitted by agricultural activities, the next chapter will review technologies presently available to measure odors qualitatively and quantitatively. It will demonstrate that the olfactometer is an instrument widely used in the measurement of odor. An entirely automated and flexible dynamic olfactometer will then be presented as it was conceived and built at the Faculty of Agricultural and Environmental Sciences of McGill University.

This paper will be submitted for publication in the **Journal of Canadian Agricultural Engineering**. **Authors: Choinière, D. and Barrington, S.F.** The contribution of the authors are: i) First author conceived, built and tested the olfactometer and collaborated in the writing of the article. ii) Second author supervised the project and co-edited the article.

CHAPTER IV

The Design of a Versatile Dynamic Olfactometer

4.1 Abstract

Odors from livestock and organic wastes are a source of annoyance jeopardizing many agricultural sectors. There is a need for precise instrumentation in odor measurement to develop and test odor control techniques and regulations. This article reviews the techniques presently available for the measurement of odors. The human nose is still the most sensitive instrument available to quantify and qualify odors. But, humans can introduce bias in the evaluation of odors.

Therefore, several olfactory methods have been developed and among them, the dynamic forced choice olfactometer is the most widely recognized. This instrument offers three sniffing ports to a panelist, one of which is contaminated with odorous air and the panelist must identify which port is contaminated. The first dilution presented is well below detection or threshold level and the strength of the odor is increased until each panelist has correctly identified the contaminated port twice in a row. The ASTM E679 method of computing the results is preferred and the odor concentration is presented in terms of the threshold dilution for 50% of the panelists. A panel of more than 8 and even 10 members is recommended for repeatable results. Before each testing session, all panel members must be rated using n-butanol.

Based on these requirements, a dynamic forced choice olfactometer was designed and built at McGill University. This olfactometer is fully automated for fast and accurate analysis of odor samples. The olfactometer has a built in n-butanol unit for the rating of each panelist before every session. This n-butanol accessory allows for the conversion of the dynamic olfactometer into an n-butanol scale olfactometer if need be. The automation of the system and the user-friendly interface allows the controller to adjust testing parameters with

sample strength and the configuration of the olfactometer with new requirements and scientific developments.

4.2 Introduction

Odor control is an important economic issue for all agricultural sectors involved in livestock production because this industry is responsible for 70% of all organic wastes produced on a dry matter basis, including domestic wastes, pulp and paper wastes and municipal wastewater sludge. This large amount of organic wastes produces important quantities of odors causing public annoyance.

Among all agricultural sectors, the swine industry is the most promising, with several provinces planning to expand their output by 20 to 100% within the next 5 years. Nevertheless, this growth program is met with strong opposition from many rural and urban communities who fear that air, soil and water pollution is at stake. Soil and water pollution can be controlled through sound manure management and spreading practices. But air pollution by odors is a more difficult matter to deal with because of its intangible nature and because of the limited research in this field.

For humans, odors are a subconscious stress rather than an illness. Odors affect the emotional state but have little impact on the physical being of humans, although these emotional stresses can present themselves as physical symptoms (Cunnick, 1995; Schiffman, 1995). Furthermore, humans are becoming more and more sensitive to odors because of their more frequent exposure to chemicals, such as food preservatives, and to drugs as for medical purposes (Schiffman, 1994). Humans feel insecure and stressed when presented with the possibility of being exposed to odors. Thus, it is impossible for humans to give an unbiased response when approached with an odor problem. Odor perceptions are subject to all kinds of sociological bias. This bias results from stress, economical insecurity and even disputes between neighbors (Thu, 1996).

Although odor control is an important issue, researchers are just starting to understand some of the controlling processes. In the field of odor control, the development of adequate instruments to measure odors has been the main draw back.

The present article will review the technologies presently available to measure the qualities of odors perceived by humans. This review will conclude that the olfactometer is the most widely used instrument for the measurement of odors, although it offers some disadvantages. A fully automated and flexible olfactometer will then be presented as conceived and built at the Faculty of Agricultural and Environmental Sciences of McGill University.

4.3 Literature Review

The gases responsible for the emanation of odors have been quantified and identified well before the 1980's. It became obvious at a very early stage of research that the perception of odors by the human nose was far more complex than expected. A mixture of gases exerts a synergetic effect on the response of the human olfactory sense.

O'Neill and Phillips (1992) published a summary of all odorous gases identified by GC and associated with livestock manure. The human olfactory sense is especially sensitive to thiols and phenolic compounds with a sulfur group. The thiols are detected by the human nose at a concentration of 0.01 ng/m^3 or at a dilution of 10^{-14} . Hydrogen sulfide is detected at a threshold of 0.10 ng/m^3 or at a dilution of 10^{-13} . Ammonia is one of the least odorous compounds, being detected at a threshold of $2 \text{ } \mu\text{g/m}^3$ or at a dilution of 10^{-9} .

Not only has the GC been instrumental in identifying and quantifying odorous gases emitted by livestock manure, but it has been instrumental in demonstrating that the human nose can differentiate compounds of very close chemical composition, such as isomers. For example, the human nose differentiates the smell of vanilla and cresol where the basis molecular structure is a phenol with, for vanilla, an

OH, COH and OCH₃ group and for cresol, an OH and CH₃ group. The human nose detects p-cresol at a concentration of 0.05 ng/m³, m-cresol at a concentration of 0.22 ng/m³ and o-cresol at a concentration of 0.4 ng/m³ or at a dilution of 10⁻¹⁵.

The following sections will review the instruments developed to quantify and identify odorous gases as well as their capability of representing the human olfactory response.

4.3.1 Gas Chromatography to Measure Odors

Gas chromatography (GC) is the oldest but most rapid and powerful technique capable of quantifying and identifying odorous gases (Furniss *et al.*, 1989). It works by partitioning components between a mobile phase and a stationary liquid phase retained as a surface layer on a suitable solid supporting medium. The separation system is contained within a column, 2 to 30 m in length and 0.50 to 4 mm in diameter and this column is held at a constant temperature. The choice of stationary phase for the column will be influenced by the polar character of the compounds to be separated.

As the human nose, the GC is capable of differentiating between isomers and compounds with different radicals. The GC separates such compounds through the use of chiral substances or absorbents (March, 1992).

The GC offers specific disadvantages in odorous gas analysis. It is often impossible to identify all the compounds detected (Hammond and Smith, 1981). The GC is also unable to measure the synergetic effects of mixtures of gases. Non odorous gases such as those with a hydroxyl radical, contribute to odors by chemical reactions or by enhancing ionization (Harrisson *et al.*, 1991). Each compound has its own individual characteristics which, when mixed with other gases, form a new odor. For example, 4-methyl phenol is known to increase the malodor level of a mixture and skatole is known to modify the nature of the odor (Dravnieks, 1985; Barth *et al.*, 1984). Finally,

accurate CG analyzes are difficult to carry out in the field even with portable units (Kerfoot *et al.*, 1990).

Direct measurement of odorous gases by GC is difficult because of the low concentrations often encountered (Schaefer, 1977). The human nose will recognize some compounds at concentrations as low as 0.01 ng/m^3 . Thus, pre-concentration of the components of an odorous air sample is highly recommended. The volatile organic compounds can be absorbed by silica and carbon and de-sorbed using a solvent. Often, solvent recovery is incomplete and the level of solvent recovery must be measured before hand (Driscoll, 1982). Extraction by freeze vacuum techniques is an improvement over solvent extraction for chicken and pig slurry odors (Yasuhara, 1987). Concentration by purging and trapping for wastewater samples gives an excellent representation of odorous components released since the technique releases especially those gases insoluble in water (Driss and Bouguerra, 1991).

Despite the lack of insensitivity for synergetic effects, GC and CG-MS continue to be a standard analytical procedure accompanying all other technique for odor analysis.

4.3.2 Electro-chemical Cells and the Measurement of Odors

Several sensors have been developed to detect gaseous components in ambient air. These are either metal oxide semi-conductor capacitors, chemically modified field-effect transistors, optical devices and piezo-electronic quartz crystal devices (Sweeten, 1995). While some gases can be detected by one sensor, other more complex odorant such as pyridine, require multiple sensors with overlapping sensitivity (MacKay-Sim, 1992).

Photo-ionization techniques have also been used to detect air contaminants. These are sensors where air components are excited photo-electronically and the number of excited molecules is measured. This technique is less disturbed by relative humidity than the electronic sensors but the instrument must be zeroed before taking any

measurements and this may cause problems where no reference air is available. For example, to compare the odor level of two piggeries where air quality may vary between rooms and outside the room, a reference air sample may be difficult to obtain.

These electronic techniques offer the advantage of being portable devices, capable of measuring odors on site as major odor components are known to be chemically unstable (Hobbs *et al.*, 1995). The materials making up these electronic devices react with the air components and lose their sensitivity with time. Thus, they have to be replaced regularly, adding to their cost.

Hobbs *et al.* (1995) tested a photo-ionizing detector (PID) and an electronic nose (EN) against olfactometry for the detection of pig and chicken manure odors. PID had a linear response ratio to odor concentration (OC) and did not react to samples with a relative humidity exceeding 50%. Odor concentration is measured in terms of number of dilutions required to obtain a detection threshold by the human olfactory sense. OC is defined as the number of dilutions required for 50% of panel members to detect an odor and is expressed in OU/m³. PID gave a signal down to 1 000 OU/m³ but could not distinguish odors. It could detect some compounds down to µg/m³. The EN was found to respond selectively to different types of odor components but to be less sensitive than PID. Moisture interference occurred with relative humidity above 40% and the response ratio was not linear with OC. A zero reading was obtained at 60 000 OU/m³.

In general, electronic sensors are ideal for on site measurements but their sensitivity and selectivity for specific odors are inferior to those of the human olfactory sense.

4.3.3 The Olfactometer

The human nose is still the most sensitive instrument available to measure odors (ASHRAE, 1993). Not only can it detect some compounds (cresol and thiol) at levels as low as 0.01 ng/m³, but it can

also perceive the synergetic effects of gases in mixtures. As a consequence, panelists have been used to measure odor intensity and offensiveness. The use of panelists to measure odors has been termed olfactometry and this technique is known to be expensive, time consuming and exposed to bias.

Olfactometry is a complex technique requiring the proper design of several operational phases: sampling and/or bagging the sample, carrying out the olfactory test and computing the results (Morrison, 1982).

Dynamic and static sampling techniques have been used. Dynamic sampling consists in transporting the panelists on site in an enclosed chamber, free of any odors, sampling the source and pumping it to the olfactometer in the control chamber for immediate analysis by the panelists. This technique limits the number of panelists because of the limited size of chamber being transported. It is also very costly and the panelists can get fatigued from traveling from one site to another. Static sampling requires the use of non-absorbing bags such as those of Mylar™, Tedlar™ or Teflon™ (Watts *et al.*, 1992). The Mylar bags are the least absorbing but are difficult to heat seal and any leakage from the bag can lead to bias results (Sweeten, 1995).

Odors are known to deteriorate rapidly. Hobbs *et al.* (1995) observed that some of the most detectable odors oxidized after 2 hours of sampling. Odors collected in sampling bags should therefore be analyzed within 8 hours of collection (O'Brien, 1995).

Once the source is sampled, the odor can be brought to the panelists for analysis. The panelists are always asked to rate the intensity of the odor, a quantitative measure, and also, they can be asked to evaluate the offensiveness of the odor, a qualitative and more subjective measure. In olfactometry, the number of panel members and the rating of the panelists before testing are two main issues affecting repeatability of the results. Most procedures recommend the use of

more than 8 panelists (ASTM, 1981; Dravnieks *et al.*, 1986). Nicell (1994) and Nicell and Tsakaloyannis (1997) refer to 10 panelists for repeatability. The rating procedure requires the panelists to determine the threshold dilution of a clean air sample containing n-butanol. Most procedures require the elimination of the extremely sensitive and insensitive panelists.

The olfactometry procedure can then be direct or by dilution to its threshold level. Two basic direct methods have been developed: one where the air sample is passed through cotton or fabric swaths and the panelists are asked to smell the swaths and evaluate the intensity of the odor (Miner and Licht, 1981). The other technique requires the panelists to smell the samples themselves, and again evaluate their odor intensity. The rating procedure recommended for the direct evaluation of odors uses a scale of 0 to 10 where 0 pertains to no odors and 10 to a very intense odor (Bulley and Phillips, 1980). Barrington and El Moueddeb (1995) have recommended to use a scale of 0 to 5 because panelists have some difficulty in differentiating between more than 5 levels. These direct methods are exposed to a bias evaluation from the panelists. A panelist may fail to recognize a treatment reducing odor levels simply because of an aversion for the odor itself (Barrington and El Moueddeb, 1995).

To reduce bias, a butanol scale olfactometer has been designed for the direct evaluation of samples. This olfactometer has a sniffing port through which n-butanol is released in clean air at various concentrations. The undiluted odor sample is introduced through another sniffing port. The panelist is asked to state whether or not the n-butanol concentration is stronger or weaker than that of the odor sample. The odor intensity of the sample is then expressed in terms of smell intensity, SI:

$$SI = k C n \quad (\text{equation 1})$$

where

k and n = 0.261 and 0.66 for n-butanol,

C = concentration of n-butanol corresponding to the odor sample.

Sweeten *et al.*, (1983) tested the performance of the n-butanol scale olfactometer with 8 levels of n-butanol (1.5 to 80 ppm), using livestock odors. The lowest standard deviation (SD) among panelists was obtained when the n-butanol levels were presented randomly, otherwise, the panelists tended to anticipate the result. Also, panelists must be trained before using the n-butanol olfactometer. A panel of 8 members is recommended and the stimulus flow rate of the nose piece must be standardized (ASTM, 1981). For field experiments, the n-butanol reservoir must be held perfectly horizontal and at constant temperature otherwise the n-butanol concentration may vary among tests.

Odor concentration is also measured in terms of the number of dilutions required to reach the detection threshold level. The dynamic olfactometer is an apparatus used to measure diluted odors. It consists of one, two or three ports, where one port releases clean air contaminated by a specific concentration of odor sample. The first dilution is well below the threshold value and the dilution is reduced in sequence until the panelist can detect the odor. Where the panelists is presented with one port, he/she must answer yes or no, referring to the detection of the odor. To reduce bias, the olfactometer can offer two or three ports, where only one unknown port releases the contaminated air. The panelists must correctly identify the contaminated port. This apparatus is called the dynamic forced choice olfactometer (ASTM, 1979). It is the most widely used and recognized olfactometer for the measurement of livestock and organic waste odors (Sweeten, 1995).

For both types of olfactometers, the single or multiple port increasing the strength of the odor is achieved in equal steps. Normally, a panelist changes its response from pure guess to clear

perception in a 2 fold increase in concentration. Using a step under 2 takes more time and above 3 leads to a loss of precision (Dravnieks *et al.*, 1986).

Once the odor has been evaluated, the results need computing into a practical form. For the n-butanol scale olfactometer, the selected concentration is used to compute the SI value (equation 1). For the threshold olfactometer, the OC is presented as the logarithmic values of the number of dilutions at the threshold, namely the log (Z) value. Three methods have been designed to compute a dilution threshold from the response of the panelist (Dravnieks *et al.*, 1986):

1) The ASTM E679 method giving a practical value close to that concentration for which $p=0.5$. The value used is a geometric mean of the concentration in 2 triangles, one in which the panelist made the last wrong answer and the other in which the panelist made, for the first time, two consecutive right answers.

2) The Hall-Ellis Quantal Response Method proposed for panels of less than 8 members. This method uses a ranking procedure because a log normal distribution of panelist sensitivity may not be satisfied.

3) The Odor Detectability Function According to the Signal Detection Procedure (TSD-50) which is an index of detectability, d' , obtained from the fraction of correct responses at each concentration via the use of a table.

According to Dravnieks *et al.* (1986), the TSD-50 method produces lower log (Z) values than the E679 and the Hall-Ellis methods for panels of more than 8 members. The E679 and Hall-Ellis methods gave similar results, but the Hall-Ellis method gave less scatter for panels of less than 8 members. Furthermore, the forced choice method helps reduce the panelist bias with the E679 method.

Nicell *et al.* (1986) introduced the concept of a discrimination

threshold to improve result repeatability by accounting for the effects of chance in evaluating the individual panelist's threshold. This threshold is a multiple of the actual detected threshold, as computed by the E679 method but included a factor accounting for the fact that the panelist may still have been guessing during his/her last right answers and that the geometric mean is an approximation of the true response. Nicell *et al.* (1986) also demonstrated the effect of selecting panelists which are either extremely sensitive or insensitive to odors. For a panel made up of 10 members, such a person can change the detection level by more than 25%. Nicell *et al.* (1986) suggested guidelines for repeatable results (a variability of 10% or less between repetitions) is to limit the effect of one panel member on the over all results. A panel size of 10 members is preferable and all panelists with an extreme sensitivity (threshold detection level of more than 2 dilution steps over or above that of the other panelists) should be eliminated.

To improve the repeatability of results, O'Brien (1996) recommended asking the panelists whether or not they were guessing, inkling or certain of their port selection. Based on this comments, the dilution threshold can be reported as being either that of detection or recognition.

In summary, the most widely recognized and used technique for the measurement of livestock and organic waste odors is the dynamic forced choice olfactometer. The n-butanol scale olfactometer is also used but to a more limited extent. The dynamic olfactometer requires that all panelists be rated with n-butanol before each trial. The ASTM E679 method for computing OC is also the most widely accepted because of its reliability and ease of application. To improve the repeatability of the results, either the discrimination threshold should be used or the panelists should be asked whether or not they are guessing.

From this review, a dynamic forced-choice olfactometer was designed and built. The unit was fully automated to reduce chances of errors while setting the dilution levels and to speed up the process. The

olfactometer was also equipped with a bottle of n-butanol to automatically rate all panelists before each test and to convert the olfactometer into an n-butanol scale olfactometer if need be. The following sections present the olfactometer and its conception basis.

4.4 Conception Basis For a Dynamic Olfactometer

The dynamic olfactometer is the most widely accepted method of evaluating the strength of an odor or the number of dilutions required before a human being can detect its presence (Sweeten, 1995). Two recognized associations have produced standards on the construction requirements of olfactometers : ASTM (American Society of Testing of Materials, 1991) and CEN (Comité Européen de Normalisation, 1995). The following discussions will summarize their requirements. In building the McGill olfactometer, the standards of the Montréal Urban Community (MUC) have been used, along with those of ASTM and CEN. The MUC operates an air quality laboratory dealing with odor complaints.

A dynamic olfactometer must be so designed as to obtain an unbiased response from a panelist. To achieve this, the olfactometer must offer three air ports to a panelist, one of which is contaminated by an odorous air sample. Thus, the panelist must try to detect the air port which is contaminated. The olfactometer is operated in such a way as to present the panelists with a sample of contaminated air at such a small dilution rate that the panelist cannot detect it. The level of contaminated air is then increased by a factor of 1.4 to 2.4 until the panelist identifies the port with the contaminated air (ASTM, 1991). Before a correct answer is recorded, the panelist must identify the correct port twice in a row. The panelist can then be asked to rate the offensiveness of the contaminated air.

The dynamic olfactometer must be built in such a way as to avoid any foul air contamination. Thus, it must be built of materials which absorbing very limited amounts of odor. The materials most recommended are: Teflon™ and Tedlar™ by Dupont, stainless steel, glass

and Nalophan™ by Hoechst.

The length of tubing used must be limited, to reduce the contamination of the system constituting the dynamic olfactometer. The orifices must be as large as possible to prevent blocking. Temperature changes exceeding 3°C must be prevented to minimize airflow discrepancies.

The dynamic olfactometer must be able to dilute air samples from 2^7 to 2^{14} with a minimum dilution range of 2^{13} between the smallest and largest dilution capabilities. The air sample can be diluted in the sampling bag by pumping a known amount of clean air into the bags before sampling the contaminated air. The dynamic olfactometer must also be able to decrease the dilution by a step factor of 1.4 to 2.4 between each dilution (ASTM, 1991). Generally, a step factor of 2 is used. The dilutions must be presented to the panelist in an ascending order, thus by increasing the strength of the odor.

The air ports presented to the panelists must be especially designed for sniffing. The airflow from the port must be higher than that of the panelist's nose to prevent sample dilution by the ambient air, but must present a barely perceptible face velocity. The CEN (1995) recommends an airflow of 20 l/min at a speed out of the air port of 0.2 to 0.5 m/s. According to O'Brien *et al.* (1996), the most repeatable results are obtained with air flow rates of 10 to 20 l/min, with face velocities ranging between 0.01 and 0.1 m/s and for nose cup diameters of 4.7 and 9.5 cm. The larger nose cups tend to require a higher air flow for repeatable results. The airports must offer a constant air distribution over their entire surface, with a tolerable variation of 10%. The air ports must be identical as to offer no choice to the panelist.

4.5 The Conception of The McGill Olfactometer

The McGill olfactometer was built according to the specifications of ASTM (1991), CEN (1995) and the MUC. It offers the following criteria.

The McGill olfactometer can seat 6 panelists at once. According to the MUC, it takes 6 panelists to obtain repeatable results. Other researchers prefer 10 panelists (Nicell, 1994). If ten or more panelists are required for a specific study, the olfactometer evaluation can then be repeated using two or more sets of 6 panelists. The olfactometer has an octagonal seating arrangement to minimize the length of tubing, but also to reach each evaluation panel from a central distribution point, with the same length of tubing (Figure 4.1). Each panelist has three buttons, A, B and C, to select the contaminated port, and a slider to evaluate the offensiveness of the odor once recognized. The frequency used to record the response of the panelists is 10 Hz.

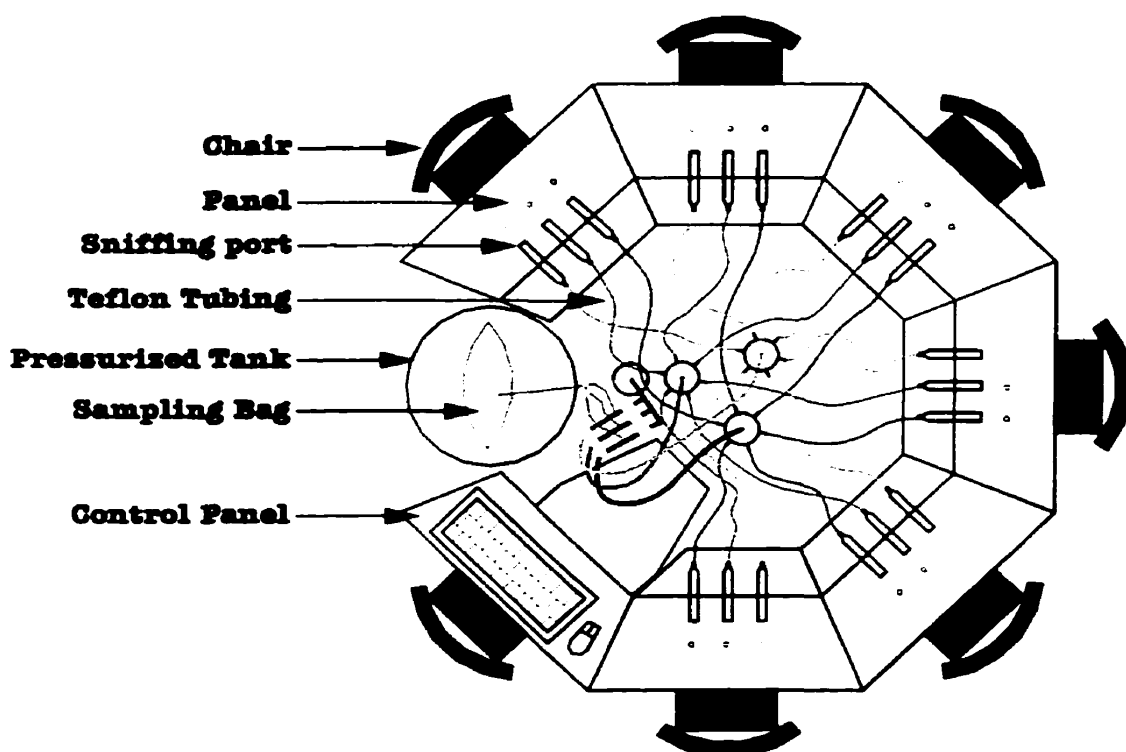


Figure 4.1 The octagonal arrangement of the system

The olfactometer distributes the air into three main lines using precision rotameters with an accuracy of 5%. The electronic mass flow controllers used to select the range of foul air dilution offer an accuracy of 2%. The airflow rate to each port is 20 l/min but it can be adjusted manually between 10 to 25 l/min. The olfactometer can dilute the

contaminated sample from 1:12 000 to 1:6, based on a flow rate of 20 l/min at each airport. The step factor between each dilution can be adjusted from 1.1 to 3. The instrument requires less than 5 seconds to flush the system and adjust the dilution to the required level. The olfactometer offers three different delays adjustable from 0 to 5 minutes: first, a delay between each dilution below the threshold level; second, a delay between each dilution above the threshold level; third, a delay between each air sample. ASTM (1991) recommends from 2 to 5 minutes between sniffing operations when panelists are exposed to a strong odor, to minimize their fatigue. Allowing 0.5 minutes between sniffing operations under the threshold and 2 minutes above threshold, and if 8 odor levels must be tested before exceeding the threshold level, the present olfactometer can run one sample in less than 10 minutes.

The air flow chart of the system is illustrated in Figure 4.2. The olfactometer has a built in n-butanol unit allowing for the automatic calibration of all panelists before each test. The n-butanol concentration at the outlet of the injector is $3\,450\ \mu\text{L}/\text{m}^3$. The olfactometer is conceived to calibrate the panelists using a range of n-butanol of 0.35 to $345\ \mu\text{L}/\text{m}^3$.

The olfactometer can handle four air sample bags at once. The air bags are placed in a stainless steel tank and compressed to force the contaminated air into the system. The computerized system of the olfactometer identifies the bag by the outlet it is connected to.

The entire system is fully automated. Before any test, the supervisor sets his requirements from the computer screen. Then, the panelists are seated and the computer of the system runs the entire test. The computer initially tests all panelists using n-butanol, if it is required by the supervisor. The computer stops when all panelists have correctly identified the correct n-butanol airport twice in a row. During the n-butanol evaluation, the computer is programmed to move on to the next higher dilution once the panelists have all answered. The contaminated port is randomly changed by the computer between each

dilution. Then, the computer proceeds to the evaluation of the first air sample and proceeds with the determination of the detection threshold as for the n-butanol test. In turn, the computer will test the other three air samples. The panelists can record the offensiveness of the air sample whenever they want and the computer will automatically record their observation. A slider is used for this purpose. Once the evaluation is completed, the computer prints out the results. Each panelist has a digital indicator where instructions are displayed by the computer.

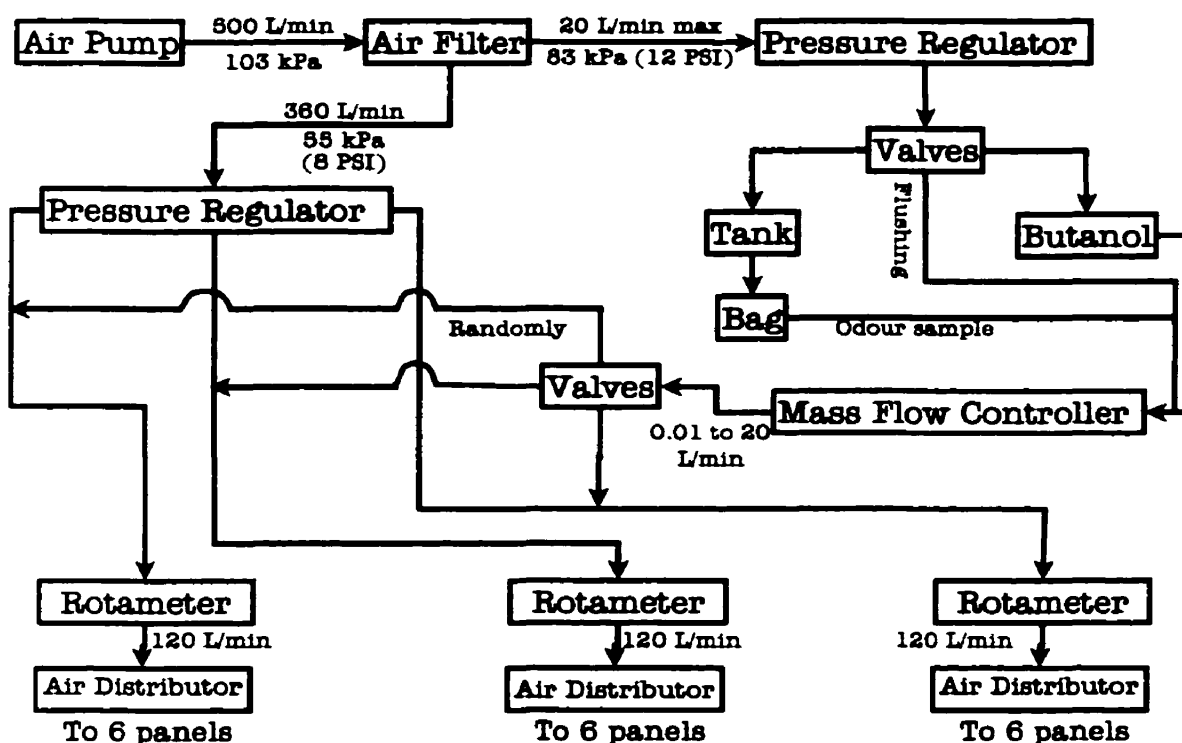


Figure 4.2 The airflow chart of the system

The computerized system is set up to record the name of the panelist and their individual n-butanol rating from one test to another. The computer system can control all tasks, such as the pump airflow, the adjustment of the settings, the flow direction, the butanol calibration and the flushing and purging operations. It records all data, such as the origin of the contaminated air sample, the time and date of

sampling and its evaluation. All information is produced on screen or can be printed out. This automation allows for the evaluation of 4 contaminated air samples with 6 panelists, within 40 minutes and depending upon the speed of the panelists. The system is also set up to compute the results according to the E670 method or the Hall-Ellis method.

Finally, the airflow was verified against a flow calibrator model Dry-Cal™ DC-1 with flow cells model Dry-Cal™ DC-1L for a flow below 1 l/min and DC-1H for a flow above 5 l/min (Dry-Cal™ by BIOS International Corp., Pompton Plains, N.J., USA). From this calibration, the maximum variation in air flow has been found to be 2% of the set flow for all the mass flow controllers. Furthermore, the flow emanating from sniffing funnels have been found to be precise within 2% of the set flow rate. Consequently, the maximum calculated error of a dilution at the sniffing port is 4%.

4.6 Summary

The McGill olfactometer is a dynamic forced choice olfactometer fully automated which is capable of calibrating the panelists and analyzing 4 contaminated air samples within 40 minutes. It seats 6 panelists but the system can be built to accommodate more panelists if need be. Most researchers prefer to use 10 panelists for repeatable results. This olfactometer is unique because of its level of automation and speed with which it can evaluate air samples. It requires the controller to input the base parameters, the name of the panelists and the sample origin. Once the panelists are seated, the computer runs the test without any further input from the controller. The results are analyzed using either the E670 method or the Hall-Ellis method and are printed or saved into the database. The n-butanol rating of each panelist is also memorized as future reference on the sensitivity of each person.

The McGill University olfactometer can be used as an n-butanol scale olfactometer if required, because it has a built in system capable

of producing n-butanol dilutions. The only limitation is the presentation of 20 l/min of undiluted contaminated sample. If such a sample must be presented for 1.5 minutes to 6 panelists, the sample volume must exceed 200 l, which represents the content of the four sample bags which the system can hold.

4.7 Acknowledgment

The McGill olfactometer was built with the collaboration of the MUC, NSERC and Shur-Gain.

4.8 References

ASHRAE. 1993. Handbook of fundamentals. American Society of Heating, Refrigeration and Air Conditioning. Atlanta, Georgia, U.S.A., 12.1-12.6.

ASTM 1981. Standard recommended practices for referencing supra-threshold odor intensity. American Society for Testing and Materials, Philadelphia, PA, USA.

ASTM 1991. Standard practice for determination of odor and taste thresholds by a forced choice ascending concentration series method of limits. E679-91. 1991 Annual Book of Standards, American Society for Testing and Materials, Philadelphia, PA, USA.

ASTM. 1979. Determination of odor and taste thresholds by forced choice ascending concentration series method of limits. E 679-79. American Society for Testing Materials, Philadelphia, PA, USA.

Barrington, S.F. and El Moueddeb, K. 1995. A direct method for the evaluation of odors. Proceeding International Conference on Livestock odors, Iowa State University, Ames, Iowa, USA, 65-69.

Barth, C.KL., Elliott, L.F. and Melvin, S.W. 1984. Using odor control technology to support animal agriculture. Transactions of the ASAE, 27(3): 859-864.

Bulley, N.R. and Phillips, D. 1980. Sensory evaluation of agricultural odors. A critical review. Canadian Agricultural Engineering,, 22(2): 107-112.

CEN. 1995. Odor Standards. CEN/TC 264N 134. Comité Européen de Normalisation, Dusseldorf, Germany.

Cunnick, J. 1995. Implications of environmental odor on psychological status and health. In: International Symposium on Livestock Odor Control. Iowa State University, Ames, Iowa, USA, 156-159.

Dravnieks, A. 1985. Atlas of odor character profiles. ASTM Committee on sensory evaluation of materials and products. ASTM data series, Baltimore, MD, USA.

Dravnieks, A., Schmidtsdorff, W. and Meilgaard, M. 1986. Odor threshold by forced choice dynamic triangle olfactometer: reproducibility and methods of calculation. Journal of the Air Pollution Control Association, 36: 900-905.

Driscoll, J.N. 1982. Identification of hydrocarbons in complex mixtures using a variable energy PID and capillary column gas chromatograph. Journal of Chromatographic Science, 20: 91-94.

Driss, M.R. and Bouguerra, M.L. 1991. Analysis of volatile organic compounds in water by purge-trap and gas chromatography. Journal of Environmental Analytical Chemistry, 45: 193-204.

Furniss, B.S., Hannaford, A.J., Smith, P.W.G. and Tatchell, A.R. 1989. Vogel's textbook of practical organic chemistry. Fifth edition. Longman House, Burnt Mill, Harlow, Essex, U.K.

Hammond, E.G and. Smith, R.J. 1981. Survey of some molecular dispersed odor constituents in swine house air. Iowa State Journal of Research, 55(4): 393-399.

Hardwick, D.C. 1986. Agricultural problems related to odor prevention and control. In : Odor prevention and control of organic sludge and livestock farming. Elsier Applied Science Publishers, London, England, 21-26.

Harrison, R.M., de Mora, S.J., Rapsomanikis, S. and Johnson, W.R. 1991. Introductory chemistry for the environmental sciences. Cambridge United Press, Cambridge, U.K., 272-275.

Hendrick, J., Vrielink, M. and van der Peet., C. 1997. Reducing ammonia emissions from pig housing by adding acid salts to the feed. International Symposium on Livestock Environment. American Society of Agricultural Engineering, St Joseph, Michigan, USA.

Hobbs, P.J., Misselbrook, T.H. and Pain, B.F. 1995. Assessment of odors from livestock wastes by a photoionization detector, an electronic nose, olfactometry and gas chromatography-mass spectroscopy. Journal of Agricultural Engineering Research, 60: 137-144.

Kerfoot, H.B., Pierret, S.L., Anik, E.N., Bottrell, J.V. and Petty, J.D. 1990. Analytical performance of four portable G.C. under field conditions. Journal of Air Quality and Waste Management Ass., 1106-1114.

MacKay-Sim, A. 1992. Electronic odor detection - problems and possibilities. In: Odor update '92, Proceedings Workshop on Agricultural Odors. MRC report Department of Agriculture of Queensland # 64/24. Department of Primary Industries, Toowoomba, Queensland.

March, J. 1992. Advanced organic chemistry. Reactions, mechanics and structure. Fourth edition, John Wiley and Sons, New York, USA.

Miner, J.R. and Licht, L.A. 1981. Fabric swatches as an aid in livestock odor evaluations. In: Livestock waste, a renewable resource. Proceedings of the 1980 International Symposium on Animal Waste. American Society of Agricultural Engineers, St Joseph, Michigan, USA, 302-305.

Morrison, G.R. 1982. Measurement of flavor threshold. *Journal of Inst. Brew*, 88: 170.

Nakamoto, T, Fudkuda, A. and Morizumi, T. 1991. Improvement of identification capability in an odor sensing system. *Sensors and actuators*, B3: 221-226.

Nicell, J.A. and Tsakaloyannis, M. 1997. A protocol for odor impact assessment. *Proceedings of the 4th International Conference on Characterization and Control of Emissions of Odors and VOCs*, Air and Waste management Association. Pittsburg, Pennsylvania. October 20-22, Montréal, Canada, 182-194.

Nicell, J. 1994. Development of the odor impact model as a regulatory strategy. *International Journal of Environment and Pollution*, 4 (1/2): 124-138.

Nicell, J.A., Gnyp, A.W. and St. Pierre, C. 1986. A mathematical analysis of odor threshold determinations. *Transactions of the Air and Waste Management Association*, Pittsburg, Pennsylvania, USA, 167-183.

Nicell, J. 1994. Development of the odor impact model as a regulatory strategy. *Int. Journal of Environment and Pollution*, 4: 124-138.

Noren, O. 1986. Design and use of biofilters for livestock buildings. In: *Odor prevention and control of organic sludge and livestock farming*. Elsier Applied Science Publishers, London, England, 234-238.

O'Brien, M.A. 1993. Guidelines for odor sampling and measurement by dynamic dilution olfactometry. EE-6 subcommittee on the standardization of odor measurement, Air and Waste Management Association. Pittsburg, PA.

O'Brien, M.A. 1995. Revised guidelines for odor sampling and measurement by dynamic dilution olfactometry. EE-6 subcommittee on the standardization of odor measurement, Air and Waste Management Association. Pittsburg, PA, USA.

O'Brien, M.A., Duffee, R.A. and Ostojic, N. 1996. Effect of sample flow rate in the determination of odour threshold. EE-6 subcommittee on the standardization of odor measurement, Air and Waste Management Association. Pittsburg, PA, USA.

O'Neill, D.H. and Phillips, V.R. 1992. A review of the control of odor nuisance from livestock buildings: Part 3, Properties of the odorous substances which have been identified in livestock wastes or in the air around them. *Journal of Agricultural Engineering Research*, 53: 23-50.

Patni, N.K. and Jui, P.Y. 1993. Effectiveness of manure additives. Paper no. 934021. ASAE, St Joseph Michigan, USA.

Ritter, W. F. 1989. Odor control of livestock wastes : State-of-the-art in North America. *Journal of Agricultural Engineering Research* 42: 51-62.

Schaefer, J. 1977. Sampling characterization and analysis of malodors. *Agric. and Env.*, 3: 121-127.

Schiffman, S. 1995. The effects of environmental odor emanating from commercial swine operations on the mood of nearby residents. *Brain Research Bulletin*, 37(4): 369-375.

Schiffman, S. 1994. Physiological effects of swine odors on humans. In: Round Table Discussion on Odor Control, Iowa University, Ames, Iowa, USA, 87-92.

Shurme, H.V. 1990. Basic limitations for an electronic nose. *Sensors and Actuators*, B1, 48-53.

Sobel, A.T., Ludington, D.C. and Yow, K.V. 1988. Altering dairy manure characteristics for the solid handling by the addition of bedding. *Journal of Soil and Water Conservation*, 9: 132-137.

Sorel, J.E., Gauntt, R.O., Sweeten, J.M., Reddell, D.L. and McFarland, A.R. 1983. Design of a 1-butanol scale dynamic olfactometer for ambient odor measurements. *Transactions of the ASAE*, 26(04): 1201-1205.

Spoelstra, S.F. 1980. Origin of objectionable odorous components in piggery wastes and the possibility of applying indicator components for studying odor development. *Agriculture and Environment*, 5: 241-260.

Sweeten, J.M. 1995. Odor measurement technology and applications: a state of the art review. In: *Seventh International Symposium on Agricultural and Food Processing Wastes*. ASAE, St Joseph, Michigan, USA, 214-229.

Sweeten, J.M., Reddell, D.L. and McFarland, A.R. 1983. Field measurement of ambient odors with a butanol olfactometer. *Transactions of the ASAE*, 26(04): 1206-1216.

Tandem Trade Corporation. 1995. Personal conversation with Mr. Paul Jourdain. Evelyn Avenue, Toronto, Canada.

Thu, K., DeLind, L., Durrenberger, E.P., Flora, C, Flora, J., Heffernan, W. and Padgett, S. 1995. Social issues. In: *Understanding the impact of large-scale swine production. Proceedings from an Interdisciplinary Scientific Workshop*. North Central Center for Rural Development, The University of Iowa, Des Moines, Iowa, USA.

Watts, P.J., Jones, M. Lott, S.C., Tucker, S.W. and Smith, R.J. 1992. Odor measurement at a Queensland Feedlot. ASAE paper 92-4516. American Society of Agricultural Engineering, St Joseph, Michigan, USA.

Yasuhara, A.J. 1987. Identification of volatile compounds in poultry manure by GC-MS. *Journal of Chromatographic Science*, 25: 371-378.

CHAPTER V

General Conclusion

The environmental impact of the swine industry is closely related to the volume of feces produced by pigs and the concentration of its undigested nutrients. Smaller volumes of and less concentrated manures will reduce the problem related to land disposal, over fertilization, and soil and water contamination. Also, potential odor production and gas volatilization will be decreased. Thus, the most logical way to find a sustainable solution is by attacking the problem at its source, for instance, by improving the feed efficiency of the pig.

The present research showed that zeolite (77% clinoptilolite) supplemented in grower hog rations improves feed efficiency. Zeolite has been shown to be significantly beneficial when fed at a level of 2% to pigs weighing up to 40 kg, when compared to a similar ration having the same energy and crude protein levels. Zeolite at level of 5% increases the feed efficiency and decreases the average daily consumption without affecting the rate of gain of pigs weighing more than 50 kg. Thus, by using a zeolite supplement at a level increasing from 2 to 5% with the weight of the pigs, it is possible to reduce feed consumption by 13.5 kg per finished hogs. This represents a 5.8% reduction in feed consumption during the growing-finishing phase. It also decreases the environmental impact of swine productions by decreasing the amount of manure produced. Also, zeolite tends to affect positively, but not significantly, the carcass quality of slaughtered pigs for carcasses weighing less than 85 kg.

When comparing the room where hogs were receiving the control feed containing sand and that where hogs were fed the zeolite feed, no significant differences in ammonia levels were found. However, diluting the pig's feed with 2 or 5% of zeolite or sand reduced the ammonia level in the air of both rooms. Thus, it is possible to reduce the ammonia

level inside farm buildings by reducing the crude protein level of the feed. Very low levels of hydrogen sulphide were measured throughout the experiment in both rooms. The level of carbon dioxide was not significantly different for both rooms. However, carbon dioxide was directly affected by the ventilation rate. Nonetheless, panelists found that the odor level of the zeolite room was slightly less with the 2% zeolite than that of the control room, but there was no difference with 5% zeolite. The management and design of the ventilation system, the ventilation rate, the cleanliness of the room and feed crude protein had more significant effects on air quality and odor level inside the grower rooms than the use of zeolite.

Finally, an automated dynamic olfactometer was conceived and built, based on the forced choice triangular method. This apparatus is innovative by its level of automation, its simplicity of operation, its rapidity of execution and its level of precision. In fact, the olfactometer can calibrate six panelists simultaneously with n-butanol and evaluate 4 different odor samples within 40 minutes. The user only needs to enter the required parameter on the setup wizard of the Windows oriented control software. All other tasks are automatically performed by the olfactometer itself. The database oriented software allows the user to print the results after the test or to keep them for further consultation. The built-in butanol injector removes the need of preparing butanol samples for quick and easy calibration of panelist. This injector allows one to transform the olfactometer in a n-butanol scale olfactometer, if need be. The olfactometer is a good tool to measure odors in the agricultural sector.

5.1 Recommendations for Future Research

The present research has demonstrated that zeolite has the potential to reduce the environmental impact of the swine industry by increasing the animals' feed efficiency. Nevertheless, further research needs to be done in order to identify its more specific effects, such as:

1. The optimal level of zeolite supplement in reference to the

animal's weight.

2. Having found and using the ideal level of zeolite in terms of the animal's weight, a large scale experiment should be conducted using an "all in all out" system. This system would provide more valuable and stronger statistical results.

3. A research investigating the effects of zeolite on the metabolisms of pigs needs to be investigated. A nutrient mass balance experiment needs to be performed using metabolism cages to better understand how pigs utilize zeolite. This research should determine the effects on manure volume and nutrient content.

4. A study on the perception of agricultural odors should be done with the olfactometer to find the detection threshold, the recognition threshold and tolerance threshold of various odors. This study should provide the information required to derive a specific dilution model for agricultural odor, taking into account the type of animals, feed, housing and manure management. This should lead to a standard for the evaluation of agricultural odors and give guidelines for a more specific and realistic regulation in this field.

5. Finally, it would be very interesting to conceive and build a new generation of swine housing facilities with all the knowledge we possess in odor control and environmental impacts associated with the swine industry. This swine housing facility should be used to verify the interactive effects on the various techniques used to reduce the soil, water and air pollution and enhance the well being of the pig, worker, neighbor and the entire community.

APPENDIX A - Statistical Model

A.1 Experimental Model

The experimental model in this project was a temporal repeated-measures ANOVA with a randomized complete block design. The experimental design was composed of four blocks with two to four replicates per treatment per block, two treatments (control and zeolite), four (bi-weekly) repeated measure and one covariable. The use of a covariable was necessary in this experiment to remove differences in the weights between groups of pigs. The covariable corresponds to the initial weights of pigs measured when the experiment started.

The blocks are there to increase the precision of the analysis. They take into account the possible spatial heterogeneity due to the gradient in air quality and the proximity of the interior access (Figure A-1).

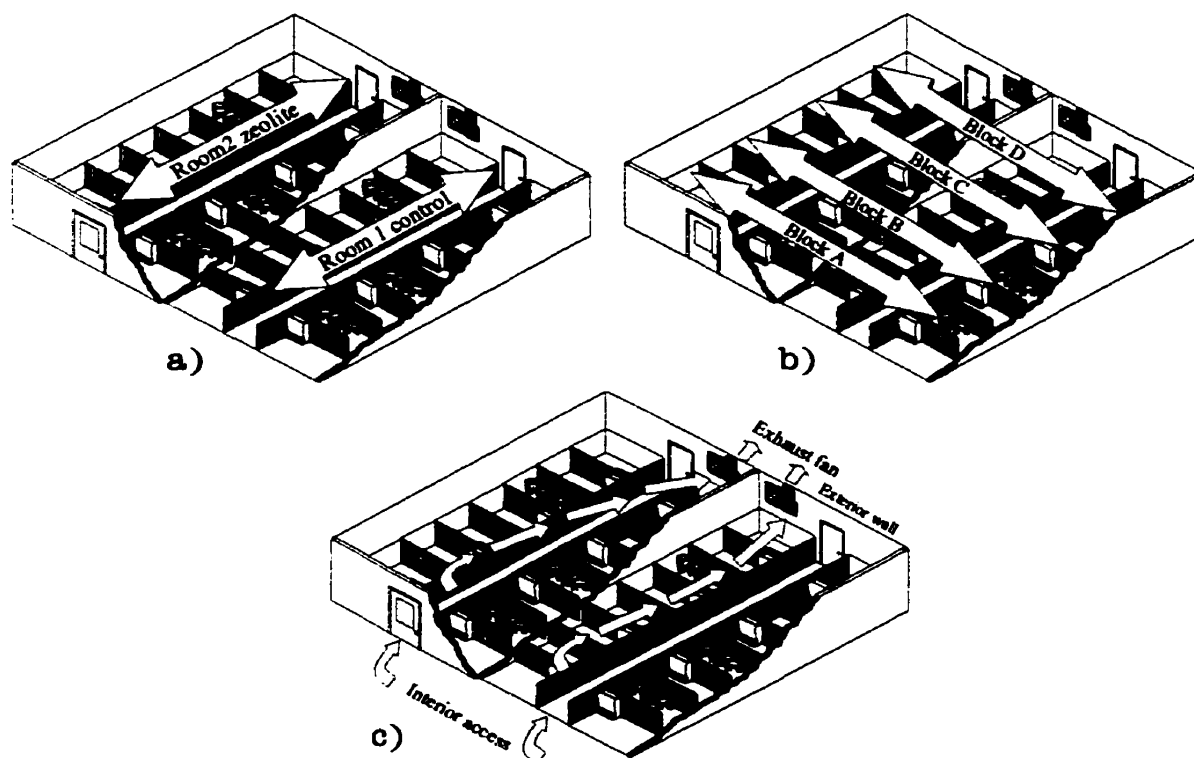


Figure A-1 Experimental layout; a) Treatment assignment, b) Block assignment, c) Ventilation flow pattern

The null hypotheses in this experiment were:

- 1) H_0 ADI : $X_{\text{control}} = X_{\text{zeolite}}$
- 2) H_0 ADG : $X_{\text{control}} = X_{\text{zeolite}}$
- 3) H_0 F/G : $X_{\text{control}} = X_{\text{zeolite}}$

In order to analyze the data correctly, it was essential to extrapolate the missing values, which were calculated with SAS (Figure C-1). The data has been verified to make sure it was normally distributed (Figure C-2). Most of the results were normally distributed except for the time X_3 of ADI in the 2% zeolite experiment. Therefore, no transformation of the data was judged necessary prior to analysis.

The analysis of variances were performed on data concerning the average daily intake, the average daily gain and the feed/gain ratio to test the effects of zeolite for significance. The classical ANOVA, the modified ANOVA and the MANOVA were three analyzes performed with SAS (Figure C-3) to test the null hypotheses. The significance levels were determined according to Wilks' criterion and the F-values were considered significant when the probability level was less than 0.05.

A.2 Classical ANOVA

In this experiment, the classical ANOVA model analyzes variances in the feed/gain ratio, average daily gain and average daily intake of pigs under two treatments. The classical ANOVA model is described as:

$$X_{ij} = \mu + a_i + B_j + (aB)_{ij} + \varepsilon_{ij}$$

with $i = 1, 2$; $j = 1, 2, 3, 4$

where μ = population mean
 a_i = treatment main effects
 B_j = block main effects
 $(aB)_{ij}$ = error term 1
 ε_{ij} = error term 2

The treatment factor is fixed and the block factor and the errors are random.

A.3 Modified ANOVA

The modified ANOVA model takes into account the correlation between the dependent variables and considers time as a factor. The time is a within-subject factor and it is crossed with treatment and with block.

The modified ANOVA model is described as:

$$X_{ijt} = \mu + b Y_{ij} + a_i + B_j + (aB)_{ij} + \Delta b_t Y_{ij} + C_t + (aC)_{it} + (BC)_{jt} + \varepsilon_{ijt}$$

with $i = 1, 2$; $j = 1, 2, 3, 4$

where μ = population mean
 $b Y_{ij}$ = covariable main effects
 a_i = treatment main effects
 B_j = block main effects
 $(aB)_{ij}$ = error term 1
 $\Delta b_t Y_{ij}$ = interaction of time t with covariable Y_{ij}
 C_t = time main effects
 $(aC)_{it}$ = interaction of treatment i with time t
 $(BC)_{jt}$ = interaction of treatment j with time t
 ε_{ijt} = error term 2

The treatment and the time factors are fixed effects and the block factor and the errors are random effects. The Greenhouse-Geisser (G-G) were used to analyze the results in this experiment.

A.4 MANOVA

The MANOVA model analyzes simultaneously the four dependent variables (X_1 , X_2 , X_3 and X_4) called vectors of observations.

The MANOVA model is described as:

$$\underline{X}_{ijt} = \underline{m} + \underline{b} Y_{ij} + \underline{a}_i + \underline{B}_j + \underline{e}_{ijt}$$

with $i = 1, 2 ; j = 1, 2, 3, 4$

where \underline{m} = multivariate intercept

$\underline{b} Y_{ij}$ = multivariate covariable main effects

\underline{a}_i = multivariate treatment main effects

\underline{B}_j = multivariate block main effects

\underline{e}_{ij} = multivariate error

The treatments are fixed effects and the block and the errors are random effects. The Wilk's Lambda test was used for the analysis.

APPENDIX B - Growth Performance Data

Table B-1 Average Daily Gain (ADG) at 2% zeolite

Treatment	Block	Covariable	\bar{x}_1	\bar{x}_2	\bar{x}_3	\bar{x}_4
C	a	21.67	0.57	0.57*	0.52	0.74
C	a	24.50	0.57	0.67	0.65	0.99
C	a	27.50	0.57	0.41	0.61	0.81
C	a	25.75	0.57	0.77	1.02	0.82
C	b	23.67	0.57	0.33	0.72	0.68
C	b	53.67	0.52	0.76	0.97	0.99
C	b	32.33	0.56	0.61	0.50	0.92
C	c	39.83	0.52	0.60	0.67	0.88
C	c	34.33	0.64	0.62	0.76	0.97
C	d	30.33	0.40	0.62	0.64	0.77
Z	a	27.00	0.66	0.59	0.83	0.66
Z	a	22.17	0.52	0.52*	0.70	0.75
Z	a	24.67	0.52	0.49	0.70	0.72
Z	a	25.00	0.52	0.48	0.68	0.76
Z	b	23.67	0.52	0.58	0.78	0.67
Z	b	56.50	0.75	0.66	0.97*	0.96
Z	b	32.50	0.52	0.56	0.59	0.73
Z	c	40.67	0.66	0.60	0.86	0.94
Z	c	34.50	0.60	0.49	0.76*	0.69
Z	d	32.50	0.71	0.51	0.76	0.51

Note: the stricken column has been removed from the statistical analysis due to the excessive number of missing data.

Table B-2 Average Daily Intake (ADI) at 2% zeolite

Treatment	Block	Covariable	\bar{x}_1	\bar{x}_2	\bar{x}_3	\bar{x}_4
C	a	21.67	1.34	1.34*	1.53	1.96
C	a	24.50	1.34	1.50	1.86	2.41
C	a	27.50	1.34	1.28	1.70	2.15
C	a	25.75	1.34	1.71	2.32	2.48
C	b	23.67	1.34	1.21	1.73	1.87
C	b	53.67	1.74	2.42	3.03	3.17
C	b	32.33	1.36	1.78	1.86	2.22
C	c	39.83	1.70	1.84	2.17	2.65
C	c	34.33	1.48	1.75	2.19	2.74
C	d	30.33	1.10	1.61	1.88	2.03
Z	a	27.00	1.17	1.38	2.02	2.18
Z	a	22.17	1.13	1.13*	1.67	1.99
Z	a	24.67	1.13	1.28	1.80	2.04
Z	a	25.00	1.13	0.98	1.80	2.05
Z	b	23.67	1.13	1.32	1.79	2.03
Z	b	56.50	1.98	2.09	3.11*	3.76
Z	b	32.50	1.13	1.53	1.93	2.17
Z	c	40.67	1.78	1.80	2.57	3.04
Z	c	34.50	1.46	1.45	2.16*	2.26
Z	d	32.50	1.19	1.44	2.02	1.83

Note: the stricken column as been remove from the statistical analysis due to the excessive number of missing data.

Table B-3 Feed to Gain ratio (F/G) at 2% zeolite

Treatment	Block	Covariable	\bar{x}_1	\bar{x}_2	\bar{x}_3	\bar{x}_4
C	a	2167	 	2.48*	2.91	2.64
C	a	24.50	 	2.22	2.83	2.41
C	a	27.50	 	3.10	2.77	2.63
C	a	25.75	 	2.22	2.27	3.03
C	b	23.67	 	3.68	2.38	2.73
C	b	53.67	3.35	3.16	3.11	3.17
C	b	32.33	2.43	2.91	3.66	2.39
C	c	39.83	3.26	3.06	3.22	2.99
C	c	34.33	2.29	2.80	2.86	2.81
C	d	30.33	2.76	2.60	2.91	2.63
Z	a	2700	1.75	2.33	2.42	3.28
Z	a	22.17	 	2.26	2.38	2.62
Z	a	24.67	 	2.60	2.56	2.83
Z	a	25.00	 	2.02	2.64	2.68
Z	b	23.67	 	2.24	2.29	2.99
Z	b	56.50	3.68	3.14	3.27*	3.87
Z	b	32.5	 	2.69	3.23	2.94
Z	c	40.67	2.68	3.00	2.97	3.22
Z	c	34.50	2.41	2.94	2.82*	3.28
Z	d	32.50	1.67	2.80	2.63	3.56

Note: the stricken column as been remove from the statistical analysis due to the excessive number of missing data.

Table B-4 Average Daily Gain (ADG) at 5% zeolite

Treatment	Block	Covariable	\bar{x}_1	\bar{x}_2	\bar{x}_3	\bar{x}_4
C	b	45.30	0.70	0.76	0.75	0.63
C	b	50.05	0.65	0.82	0.53	0.74
C	b	61.72	0.71	0.97	0.80	0.67*
C	c	48.27	0.72	0.85	0.70	0.57
C	c	44.68	0.56	0.68	0.55	0.53
C	c	60.30	0.64	0.82	0.77	0.59
C	c	43.97	0.59	0.86	0.64*	0.69
C	d	51.98	0.65	0.63	0.65	0.71
Z	b	81.60	0.81	0.64	0.92	0.84*
Z	b	41.50	0.82*	0.77	0.74	0.68
Z	b	50.10	0.58	0.78	0.61	0.86
Z	b	62.67	0.69	0.72	0.73	0.82*
Z	c	47.10	0.75	0.61	0.55	0.85
Z	c	48.65	0.57	0.63	0.73*	0.83
Z	c	59.08	0.88	0.64	0.92	0.74
Z	c	45.07	0.73	0.77	0.80	0.80
Z	d	50.45	0.60	0.72	0.71	0.73

Table B-5 Average Daily Intake (ADI) at 5% zeolite

Treatment	Block	Covariable	x_1	x_2	x_3	x_4
C	b	45.30	1.86	1.99	2.24	2.20
C	b	50.05	1.96	2.30	2.06	2.28
C	b	61.72	2.29	2.88	2.95	2.53*
C	c	48.27	1.98	2.34	2.46	2.41
C	c	44.68	1.57	1.94	1.91	1.94
C	c	60.30	2.20	2.65	2.85	2.51
C	c	43.97	1.79	2.07	2.18*	2.06
C	d	51.98	2.05	1.87	2.26	2.37
Z	b	81.60	2.37	2.76	3.06	3.21*
Z	b	41.50	1.73*	2.09	2.20	2.45
Z	b	50.10	1.81	2.33	2.26	2.57
Z	b	62.67	2.27	2.32	2.76	2.83*
Z	c	47.10	1.95	1.98	2.04	2.42
Z	c	48.65	1.68	2.04	2.34*	2.54
Z	c	59.08	2.16	2.49	2.71	2.58
Z	c	45.07	1.85	2.26	2.37	2.5
Z	d	50.45	1.99	2.27	2.53	2.62

Table B-6 Feed to Gain ratio (F/G) at 5% zeolite

Treatment	Block	Covariable	x_1	x_2	x_3	x_4
C	b	45.30	2.62	2.59	2.97	3.45
C	b	50.05	2.97	2.80	3.86	3.06
C	b	61.72	3.19	2.97	3.69	3.80*
C	c	48.27	2.74	2.74	3.48	4.20
C	c	44.68	2.80	2.82	3.44	3.65
C	c	60.30	3.43	3.23	3.69	4.22
C	c	43.97	3.00	2.41	3.42*	2.95
C	d	51.98	3.11	2.93	3.47	3.31
Z	b	81.60	2.90	4.31	3.29	3.98
Z	b	41.50	2.77*	2.72	2.96	3.57
Z	b	50.10	3.07	2.95	3.69	2.97
Z	b	62.67	3.25	3.20	3.74	3.51*
Z	c	47.10	2.59	3.23	3.69	2.84
Z	c	48.65	2.94	3.22	3.26*	3.05
Z	c	59.08	2.45	3.88	2.95	3.48
Z	c	45.07	2.52	2.90	2.96	3.12
Z	d	50.45	3.30	3.15	3.53	3.56

Treatment Z Zeolite groups of pigs
 C Control groups of pigs
 Block a, b, c, d Block, the spatial heterogeneity effect (Figure A-1)
 Covariable Y Represents the average initial weight of a group of pigs
 x_1 - x_4 x Represents the two week interval where pigs are weighed
 * Missing value extrapolated by SAS (Figure C-1)

APPENDIX C - SAS Code

```
DATA FIG;  
INPUT TRT $ BLOCK $ Y X1-X4;  
CARDS;  
.  
.  
.  
;  
PROC GLM NOPRINT;  
CLASS TRT BLOCK;  
MODEL X1-X4=Y TRT BLOCK;  
OUTPUT OUT = FIGP  
      P = XP1-XP4;  
PROC PRINT DATA=FIGP;
```

Figure C-1 SAS code for the extrapolation of the missing value

```
DATA FIG;  
INPUT TRT $ BLOCK $ Y X1-X4;  
CARDS;  
.  
.  
.  
;  
PROC GLM NOPRINT;  
CLASS TRT BLOCK;  
MODEL X1-X4=Y TRT BLOCK;  
OUTPUT OUT = FIGR  
      R=XR1-XR4;  
PROC UNIVARIATE DATA=FIGR NORMAL PLOT;  
VAR XR1-XR4;
```

Figure C-2 SAS code to test the normality of the data

```
DATA FIG;  
INPUT TRT $ BLOCK $ Y X1-X4;  
CARDS;  
.  
.  
.  
;  
PROC GLM;  
CLASS TRT BLOCK;  
MODEL X1-X4=Y TRT BLOCK;  
MANOVA H=TRT;  
MANOVA H=BLOCK;  
REPEATED TIME 4 CONTRAST/SUMMARY;
```

Figure C-3 SAS code to test the hypotheses with a covariable


```

DATA FIG;
INPUT TRT $ BLOCK $ Y X1-X4;
CARDS;
.
.
.
.
.
PROC GLM;
CLASS TRT BLOCK;
MODEL X1-X4= TRT BLOCK;
MANOVA H=TRT;
MANOVA H=BLOCK;
REPEATED TIME 4 CONTRAST/SUMMARY;

```

Figure C-4 SAS code to test the hypotheses without a covariable

```

DATA FIG;
INPUT TRT $ BLOCK $ Y X1-X4;
X1=X1/Y;
X2=X2/Y;
X3=X3/Y;
X4=X4/Y;
CARDS;
.
.
.
.
.
PROC GLM;
CLASS TRT BLOCK;
MODEL X1-X4= TRT BLOCK;
MANOVA H=TRT;
MANOVA H=BLOCK;
REPEATED TIME 4 CONTRAST/SUMMARY;

```

Figure C-5 SAS code to test the hypotheses by dividing the data by a covariable

APPENDIX D - Statistical Analysis Results

Table D-1 Statistical significant levels for 2% zeolite

MODEL	ADI			ADG			F/G RATIO		
	A	B	C	A	B	C	A	B	C
NORMALITY									
XR1	ns	ns	ns	ns	ns	ns	ns	ns	ns
XR2	ns	ns	ns	ns	ns	ns	ns	ns	ns
XR3	*	ns	ns	ns	ns	ns	ns	ns	ns
MANOVA									
TRT	*	*	*	ns*	ns	*	*	*	*
BLOCK	ns	ns	*	ns	ns	ns*	ns	ns	ns
REPEATED MANOVA									
TIME	ns	**	**	ns	**	**	ns	ns	ns
TIME*Y	*			ns			ns		
TIME*TRT	*	*	*	*	ns	*	*	*	*
TIME*BLOCK	*	ns	*	ns	ns	ns	ns	ns	ns
REPEATED MANOVA BETWEEN SUBJECT									
Y	**			*			**		
TRT	ns	ns	ns	ns	ns	ns	ns	ns	ns
BLOCK	ns	ns	*	ns	ns	*	ns	*	ns
REPEATED MANOVA WITHIN SUBJECT									
TIME	ns	**	**	ns	**	**	ns	ns	ns
TIME*Y	*			ns			ns		
TIME*TRT	*	*	*	*	*	*	*	*	*
TIME*BLOCK	*	ns	**	ns	ns	ns	ns	ns	ns

Table D-2 Statistical significant levels for 5% zeolite

MODEL	ADI			ADG			F/G RATIO		
	A	B	C	A	B	C	A	B	C
NORMALITY									
XR1	ns*	ns	ns	ns	ns	ns	ns	ns	ns
XR2	ns	ns	ns	ns	ns	ns	ns	ns*	ns
XR3	ns	ns	ns	ns	ns	ns	ns	ns	ns
XR4	ns	ns	ns	ns	ns	ns	ns	ns	ns
MANOVA									
TRT	*	*	*	*	*	*	*	ns	*
BLOCK	ns	ns	ns	ns	ns*	ns	ns	ns	ns
REPEATED MANOVA									
TIME	ns	**	**	ns	ns	ns*	*	**	*
TIME*Y	ns			ns			ns		
TIME*TRT	*	ns*	*	*	*	*	*	ns*	*
TIME*BLOCK	ns	ns	ns	ns	ns	ns	ns	ns	ns
REPEATED MANOVA BETWEEN SUBJECT									
Y	**			ns*			**		
TRT	ns	ns	ns	ns	ns	ns	ns	ns	ns
BLOCK	ns	ns	ns	ns	ns	ns	ns	ns	ns
REPEATED MANOVA WITHIN SUBJECT									
TIME	ns	**	**	ns*	ns	ns	*	*	**
TIME*Y	ns			ns			ns*		
TIME*TRT	*	ns	**	*	*	*	*	*	*
TIME*BLOCK	ns	ns	ns*	ns	ns	ns	ns	ns	ns

Note: ns = not significant, * = significant at $0.001 < p < 0.05$

** = highly significant at $p < 0.001$

Model A = statistical model with covariable

B = without covariable, C = dividing by covariable